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EVALUATION OF AIR EMISSIONS FROM HAZARDOUS WASTE TREATMENT, STORAGE, AND DISPOSAL FACILITIES

by

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16. ABSTRACT

This study has examined the fugitive air emissions from landfills, surface impoundments, storage tanks, containers (drums), solvent recovery processes, and land treatment technologies at hazardous waste disposal facilities (HWDF's). The main objective of this study was to develop and demonstrate techniques for determining air emissions from the above HWDF technologies (sources). Various predictive models for estimating air emissions exist for some of these sources. These models have been identified and evaluated for applicability to select HWDF's. Sampling approaches have been identified for measuring the air emissions from these treatment, storage, and disposal operations. Procedures for the collection and qualitative and quantitative analysis of the air samples and the liquid and solid samples taken in conjunction with the air samples have also been developed. The resulting analytical data have provided general information on the level of air emissions from the sources studied. This document summarizes the findings from each of four HWDF's tested, comparing and contrasting the measured and predicted emission results and the experiences gained in using the various sampling approaches.

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FOREWORD

The Environmental Protection Agency was created because of increasing public and governmental concern about the nation's environment and its effect on the health and welfare of the American people. The complexity of the environment and the interplay among its components require a concentrated and integrated attack upon environmental problems.

The first step in seeking environmental solutions is research and development to define the problem, measure its impact and project possible remedies. Research and development is carried out continually by both industry and governmental agencies concerned with improving the environment. Much key research and development is handled by EPA's Hazardous Waste Engineering Research Laboratory. The laboratory develops new and improved technologies and systems to treat, store, and dispose hazardous waste; to remove hazardous waste and restore contaminated sites to usefulness; and to promote waste reduction and recycling. This publication is one of the products of that research--a vital communications link between the research and the user community.

This document presents the results of air emission sampling at four hazardous waste treatment, storage, and disposal facilities; and compares the field emission results to calculated emission model results. Details of the emission sources, sampling procedures, and emission models are described. The sampling procedure and emission models used in this report are experimental and should not be considered approved procedures.

The intended audience for this document includes those involved in the review of new and existing hazardous waste facilities.

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Director
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ABSTRACT

This study has examined the fugitive air emissions from landfills, surface impoundments, storage tanks, containers (drums), solvent recovery processes, and land treatment technologies at Hazardous Waste Disposal Facilities (HWDFs). The main objective of this study was to develop and demonstrate techniques for determining air emissions from the above sources. Various predictive models for estimating air emissions exist for some of these sources. These models have been identified and evaluated for applicability to select HWDFs. Sampling approaches have been identified for measuring the air emissions from these different operations. Procedures for the collection and qualitative and quantitative analysis of the air samples and the liquid and solid samples taken in conjunction with the air samples have also been developed. The resulting analytical data have provided general information on the level of air emissions from the sources studied. This document summarizes the findings from each of four HWDFs tested, comparing and contrasting the measured and predicted emission results and the experiences gained in using the various sampling approaches.

This report was submitted in fulfillment of Contract No. 68-02-3171, Task Number 63, by Radian Corporation, under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from June 1982 to June 1984, and work was completed as of June 1984.

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SECTION 1

INTRODUCTION

The Office of Solid Waste (OSW) is required, under Executive Order 12291, to conduct a Regulatory Impact Analysis (RIA) that will examine costs and benefits for various alternatives to control air emissions from the treatment, storage, and disposal operations at hazardous waste disposal facilities (HWDFs). This study has examined the fugitive air emissions from landfills, surface impoundments, storage tanks, containers (drums), solvent recovery processes, and landtreatment technologies at HWDFs.

The main objective of this study was to develop and demonstrate techniques for determining air emissions from the above HWDF technologies (sources). Various predictive models for estimating air emissions exist for some of these sources. These models have been identified and evaluated for applicability to select HWDFs. Sampling approaches have been identified for measuring the air emissions from these treatment, storage, and disposal operations. Procedures for the collection and qualitative and quantitative analysis of the air samples and the liquid and solid samples taken in conjunction with the air samples have been developed. The resulting analytical data have provided general information on the level of air emissions from the sources studied. Specific information has been presented in separate Data Volumes for each of the four sites tested[1,2,3]. This document summarizes the findings from each of these sites, comparing and contrasting the measured and predicted emission results and the experiences gained in using the various sampling approaches.

PREDICTIVE MODELS FOR COMPARISON TO AIR EMISSION MEASUREMENTS

Reviews of models for estimating air emissions from hazardous waste treatment storage and disposal facilities have been provided to EPA by Radian[4] and GCA[5]. GCA has recommended those models shown in Table 1 for use in predicting emissions from various treatment, storage, and disposal facilities. General descriptions of those models applicable to the treatment, storage, or disposal operations tested are presented in Section 5. Data were collected at the sites for input to the models. Where possible, measured values were used as input. Where measured values were not possible, input values were obtained from records, literature values, engineering estimates, etc. Section 5 discusses the procedures for obtaining the necessary inputs. Procedures for comparing and predicting emission rates are discussed in Section 6.

TABLE 1. RECOMMENDED AIR EMISSIONS MODELS FOR HAZARDOUS WASTE DISPOSAL FACILITIES

Source	Model(s)
Landfill	Farmer, et al (1978) - for Covered Landfills Thibodeaux (1980) - Landfill Equation--without internal gas generation Thibodeaux (1981) - Landfill Equation--with internal gas generation
Landtreatment	Hartley Model (1969) Thibodeaux-Hwang (1982)
Surface Impoundment	Mackay and Leinonen (1975) - Unsteady-State Predictive Model for Nonaerated Surface Impoundments Thibodeaux, Parker, and Heck (1981) - Steady-State Predictive Model for Nonaerated and Aerated Surface Impoundments
Open Tank	Thibodeaux (1980) - Aerated Surface Impoundment (ASI) Model Hwang (1970) - Activated Sludge Surface Aeration (ASSA) Model Freeman (1980) - Diffused Air Activated Sludge (DASS) Model
Storage Pile	Midwest Research Institute Emission Factor Equations for Storage Piles
Fixed Roof Tanks	API (1962), modified by TRW/EPA, Fixed Roof Tank Breathing Losses API (1962) - Fixed Roof Tank Working Losses
Floating Roof Tanks	API (1980) - Evaporation Loss from External Floating Roof Tanks EPA/API (1981) - Standing Storage Losses from External Floating Roof Tanks EPA/API (1981) - Standing Storage Losses from Internal Floating Roof Tanks

SAMPLING APPROACHES FOR MEASURING AIR EMISSIONS

The sampling approaches for measuring air emissions from treatment, storage, and disposal facilities (TSDFs) include:

- emission isolation flux chamber,
- vent sampling,
- concentration-profile,
- transect technique, and
- mass balance.

Table 2 presents the sampling approaches identified as applicable to various treatment, storage, and disposal facilities. Discussions of the sampling approaches used during testing appear in Section 4.

SAMPLING SITES

Six sites were investigated during an initial pretest site survey. The survey was designed to select those sites that had TSDFs most suitable for testing. The recommendations for field testing and results from the initial sampling and analytical efforts are found in the pretest site survey report[6]. Four of these six sites were tested, including Sites 2, 4, 5, and 6. A brief description of these sites is found in Section 3.

TESTING PROGRAM

The field testing conducted at the sites is shown in Table 3. The field testing was performed during the following periods during the Fall of 1983:

- Site 5 - September 30 - October 11,
- Site 4 - October 11 and 12,
- Site 6 - October 24-28, and
- Site 2 - November 14-18.

A systems and performance audit of the on-site sampling and analytical activities was conducted by Radian's Quality Assurance Coordinator on October 5-7 (Section 7).

TABLE 2. SUMMARY OF EMISSION MEASUREMENT APPROACHES FOR SELECTED ACTIVITIES WITHIN A HAZARDOUS WASTE DISPOSAL FACILITY

Activity	Emission Measurement Approach[a]	Comments
Treatment Plants		
1) Physical, biological and/or chemical treatment units, including continuous mixing in open tanks	Emission isolation flux chamber	Open tanks; little or no surface disturbance
	Mass balance	Batch process or steady-state operation/process
	Transect technique	Requires minimal interferences from other emission sources; applicable when surface is highly agitated
	Vent sampling	Closed tanks
2) Spraying/aeration and spray irrigation	Transect technique	Requires minimal interferences from other sources; must consider aerosol *vs.* vapor during sampling collection
3) Distillation and cracking/ refining	Vent sampling	
Storage		
4) Open tanks	See 1) above	
5) Surface impoundments	Concentration-profile technique	Must meet criteria for the micro-meteorological model
	Transect technique	Requires minimal interferences from other emission sources; not applicable to large impoundments
	Emission isolation flux chamber	Small surface impoundments and/or minimal surface disturbances
	Mass balance	Batch process or steady-state operation/process
6) Evaporation ponds or tanks (unheated and heated)	See 1) above	
7) Drum recycling operations	Transect technique	Requires minimal interferences from other emission sources
	Emission isolation flux chamber	Bagging of single drums only
8) Spent drum storage	See 7) above	
Disposal Facilities		
9) Landfills (active and inactive	Transect technique	Requires minimal interferences from other emission sources
	Emission isolation flux chamber	Covered landfill only
	Vent sampling	Covered landfill with gas collection system
10) Landtreatment	Emission isolation flux chamber	
	Mass balance	Requires some knowledge of biodegradation rate
	Transect technique	Requires minimal interferences from other emission sources
Fugitive Sources		
11) Vacuum pumps used on tank trucks	Vent sampling	
	Transect technique	Requires minimal interferences from other emission sources

[a]Description of emission measurement approaches:
Emission isolation flux chamber - direct emission measurement, no interference from other emission sources
Mass balance - indirect emission measurement based upon difference in bulk component concentrations
Transect technique - indirect emission measurement based upon ambient concentrations downwind from source, other emission sources can interfere with measurements
Vent sampling - direct emission measurement, no interferences from other emission sources
Concentration-profile technique - indirect emission measurement based upon ambient concentrations immediately above surface, minimal interference from other emission sources as long as a concentration profile can be measured

TABLE 3. SUMMARY OF FIELD TESTING PERFORMED

Site	Source	Sampling Approach	Model
2	Landfill (active)	Transect technique and Emission isolation flux chamber	No specific model applicable
	Landtreatment	Emission isolation flux chamber and Concentration-profile technique	Thibodeaux-Hwang (1982), Hartley (1969)
4	Chemical Landfill D (active)	Flux chamber	No specific model applicable
	Chemical Landfill C (inactive)	Flux chamber	No specific model applicable
5	Wastewater treatment, Reducing Lagoon 1	Flux chamber	Thibodeaux, Parker and Heck (1983)
	Wastewater treatment, Oxidizing Lagoon 2	Flux chamber	Thibodeaux, Parker and Heck (1983)
	Wastewater treatment, Holding Pond 6	Concentration-profile Flux chamber	Thibodeaux, Parker and Heck (1983)
	Hazardous, non-hazardous drum storage building	Vent sampling	No specific model applicable
	Chemical Landfill 10 (active)	Transect technique Flux chamber	Individual cells, Farmer, et al (1978) Thibodeaux (1980)
	Chemical Landfill 7 (inactive)	Flux chamber Vent sampling	No specific model applicable
6	Distillation Process	Mass balance	No specific model applicable
	Closed Tanks (vented)	Vent sampling	API/EPA (1962)
	Drum Storage and Handling[a]	Transect technique	No specific model applicable
	Spray Evaporation Pond[b]	Transect technique	No specific model applicable

[a]Testing scheduled, but not performed due to meteorological conditions; qualitative data obtained

[b]Limited testing performed due to meteorological conditions

SECTION 2

CONCLUSIONS

The field testing performed in this program has provided data on the air emission rates from a variety of sources within hazardous waste treatment, storage, and disposal facilities (TSDFs). Air emission rates were measured using various approaches and predicted using existing models. Neither the measurement approaches nor the predictive models have been validated, and as such, this program represents a demonstration of these approaches for measuring/modeling emissions from TSDF sources. The measured and predicted emission rates have been compared throughout this report as a relative comparison only. The accuracy of the measured and the predictive procedures are not established. The experiences gained during this program should, however, provide a basis for future field testing of TSDFs.

A summary of the results of the emission rate measurements from the various TSDFs tested is given in Table 4. Only the total nonmethane hydrocarbon (TNMHC) emissions are included in this table. Results are provided for both the entire surface area (kg-C/day) and per unit area (kg-C/hectare-day). The emission rates presented in the table represent an average of all the measurements for a given source. The measurements were made over a relatively short period of time and under specific process operating and meteorological conditions. For these reasons, caution should be used in attempting to extrapolate these data to sources at other TSDFs, or for longer time periods (i.e., annual averages).

The highest emissions measured at an active landfill were encountered during active dumping of the waste (23.1 kg-C/day). Emission rates were lower (1-10 kg-C/day) in areas of the landfills which did not have active dumping concurrent with the measurements. All but one of the landfills tested were very large with multiple cells. Because of the large exposed surface areas, the emissions for the total source were similar in magnitude to the surface impoundments. No measurable emissions were detected through the cover of the inactive landfills tested. Both inactive landfills did however have vents from which emissions were detected (<0.01 kg-C/day). Emissions from the vents were not constant, rather they occurred as puffs with no specific frequency of occurence.

A variety of surface impoundments were tested, including small surface area receiving ponds (high liquid concentrations) and large surface area polishing ponds (low liquid concentrations). As expected, the emissions from the receiving ponds were higher (order of magnitude) than the polishing ponds on a per surface area basis. Emissions from the total sources were more similar due to the differences in size of the ponds, with the receiving

TABLE 4. EMISSION RATES OF TOTAL NONMETHANE HYDROCARBONS FROM TSDF SOURCES MEASURED USING VARIOUS SAMPLING APPROACHES

TSDF Source	Sampling Approach	Emission Rate (Kg-C/hectare-day)	Emission Rate (Kg-C/day)
Active Landfill			
Site 5-Landfill 10	Transect Technique	3.8, 9.2[a]	9.5, 23.1
	Emission Isolation Flux Chamber	4.5[b], 13[b]	1.1[b], 8.2[b]
Site 4-Landfill D	Emission Isolation Flux Chamber	4.1[b]	1.6[b]
Site 2-Landfill Q	Emission Isolation Flux Chamber	0.8[b]	0.015[b]
Inactive Landfill			
Site 5-Landfill 7	Emission Isolation Flux Chamber	<0.1[c]	
	Vent Sampling		<0.01
Site 4-Landfill C	Emission Isolation Flux Chamber	<01.1[c]	
	Vent Sampling		<0.001
Surface Impoundments			
Site 5-Lagoon 1	Emission Isolation Flux Chamber	10	1.4
Site 5-Lagoon 2	Emission Isolation Flux Chamber	49	7.1
Site 5-Pond 6	Emission Isolation Flux Chamber	2.7	1.4
	Concentration-Profile	0.8	0.4
Site 6-Pond 3	Transect Technique	54[d]	2.7[d]
Solvent Recovery			
Site 6-1,1,1-Trichloroethane	Mass Balance	1.2%[e], 16.7%[f]	
Site 6-MEK	Mass Balance	1.1%[e]	
Landtreatment			
Site 2-Landtreatment	Emission Isolation Flux Chamber	626-53[g]	35-3[g]
	Concentration-Profile	1080-831[h]	60.5-46.5[h]

(Continued)

TABLE 4. (Continued)

TSDF Source	Sampling Approach	Emission Rate (Kg-C/hectare-day)	Emission Rate (Kg-C/day)
Drum Storage Building			
Site 5	Vent Sampling		0.2
Storage Tanks			
Site 6	Vent Sampling		<0.1[i]

[a] active dumping of waste
[b] single cell of landfill
[c] below detection limit
[d] validity of data questionable
[e] distillation losses only
[f] washing losses
[g] emission rates measured from time of spreading to two days after spreading
[h] emission rates measured from one to two days after spreading
[i] no detectable gas flow rate

ponds (1-7 kg-C/day) being somewhat higher than the polishing ponds (0.4-1.4 kg-C/day).

The highest emissions measured were for the landtreatment of oily wastes. Depending on the approach used for making the measurement and the time that the measurement was made after initial spreading of the waste, the emission rates ranged from 3-60 kg-C/day. The waste was surface spread and included daily tilling. Emissions tended to decrease rapidly following the initial application and to increase slightly with each day's tilling.

Emissions during solvent recovery operations for 1,1,1-trichloroethane and methylethylketone (MEK) were at nominally 1% of the throughput for the distillation process. Losses (emissions) during washing of the 1,1,1-trichloroethane were substantially greater (16.7%). Emissions from a drum storage building were measured at 0.2 kg-C/day. Surveys around outside drum storage areas showed measurable TNMHC concentrations, but no emission rates were determined. Measurements of the breathing losses (emissions) from fixed-roof storage tanks were attempted, but no measurable flow from the vents could be detected.

A number of field sampling techniques were used in this study including:

- emission isolation flux chamber
- transect technique
- concentration-profile technique
- vent sampling
- mass balance

As a result of the experience gained in using these techniques, several general statements on the use and limitations of each of the approaches can be made.

The emission isolation flux chamber technique was simple and straightforward to execute in the field. No specific meteorological conditions prevented sampling, with the exception of high winds during tethered operation at some ponds. Field calibration and quality control procedures were readily performed. The statistical sampling approach appears suited to the sampled ponds, landfarm, and some landfills. However, certain of the landfills were quite large and heterogeneous in nature, making the overall representativeness of the limited data obtained suspect in these cases. In general, very good correlations were observed between all components detected from the chamber and the volatile components in the corresponding liquids and solids (waste). The variability in the emission rates determined using the flux chamber was typically much less than the transect, concentration-profile, or predicted emission rates.

The transect technique required more instrumentation and was more labor intensive than the emission isolation flux chamber. The transect technique is very dependent upon and very vulnerable to ambient meteorological conditions, the physical surroundings about the measured source, and the

configuration of the source itself. During the testing periods, testing was often prevented due to unacceptable atmospheric stabilities, high/low wind speeds, variable wind direction, and wrong wind direction. Transect testing was precluded at some sites because of the proximity of obstacles which produced air turbulence and prevented proper plume formation. These experiences emphasize the extent to which meteorological dependence can escalate the cost and ability of obtaining emission data using the transect technique. In general, the uncertainty associated with the emission rates estimated by the transect technique are greater than those measured by other methods.

The concentration-profile technique required the most instrumentation and was the most labor intensive of the three sampling approaches. It too is dependent on ambient meteorological conditions and physical configuration of the source. During the field testing, unsatisfactory meteorological conditions resulted in several days' delay and, in some cases, samples of questionable validity. Both the concentration-profile and transect techniques require analysis of air samples which are at least an order of magnitude more dilute than corresponding flux chamber samples. This fact impacts the analytical procedures which can be used with these approaches and the level of compounds which may be detected. The method is also limited to flat, relatively large area sources. The variability in the emission rates determined using the concentration-profile technique was typically greater than with the flux chamber, but better than the transect technique.

It is generally expected that the flux chamber will result in lower measured emission rate than the concentration-profile technique, due to the absence of wind effects in the flux chamber. In comparing the emission rates determined by both methods at the landtreatment area, Site 2, the concentration-profile values were indeed higher than the flux chamber values. The difference, however, may have also been due in part to the time dependence of the emission rates from the landtreatment area and the fact that the concentration-profile measurements were made following tilling (which is expected to temporarily increase the emission rate).

In contrast, at Holding Pond 6, Site 5, the flux chamber technique resulted in a statistically significant greater air emission rate than was determined by the concentration-profile technique. This phenomenon was not expected, and no explanation is available for this behavior.

As a result of the field studies, the emission isolation flux chamber sampling procedure would appear to be the preferred method of the three sampling methods which were used. It is recommended wherever it is applicable. Situations where the flux chamber may not be applicable are large areas in which some continuing activity is occurring (spreading/tilling of sludge at landtreatment sites, highly agitated surface impoundments, etc.). In these cases, the concentration-profile technique is preferred (even though it is labor-intensive and requires the most instrumentation) for large, relatively flat sources. The transect method is the third choice for

those cases where neither the flux chamber nor the concentration-profile are applicable.

The vent sampling techniques which were applied at the test sites were simple and straightforward. However, the low flow rates and intermittent nature of the emissions from both the landfill vents and storage tanks presented problems. These problems were most severe for the storage tank vents, where the velocity was undetectably low. If such sampling is to be done in the future, special apparatus will have to be designed to accurately monitor very low flow rates. Alternatively, a flux chamber could be sealed over the vent and the emissions monitored continuously over a period of time (days).

The mass balances made during the solvent purification runs resulted in a measurable loss, which was attributed to emissions. However, the precision of the calculated emission rate (mass loss) was quite poor. This imprecision is primarily attributed to the imprecision in the liquid level measurements, as well as to the fact that the calculated emission rate is the difference between two large numbers.

The Thibodeaux, Parker, and Heck air emission model was used to predict emissions from Lagoons 1 and 2 and Holding Pond 6 at Site 5. Predicted emissions were compared to emission rates for Lagoons 1 and 2 measured using the flux chamber. No statistically significant differences were determined between predicted and measured emission rates in half of the cases examined for Lagoon 1. In all other cases, the predicted rate was greater than the measured rate for Lagoon 1. For Lagoon 2, the predicted rate was orders of magnitude greater than the measured rate in all cases. This discrepancy is attributed to problems in modeling the sludge/oil/aqueous surface encountered for this lagoon. Predicted emissions were compared to emission rates for Holding Pond 6 measured using both concentration-profile and flux chamber techniques. In general, the predicted rates are statistically greater than those measured by the concentration-profile technique and less than those measured by the flux chamber.

The Thibodeaux, Parker, and Heck air emission model was also used to predict emissions from the spray evaporation pond at Site 6 due to vaporization of the liquid surface. The model does not include emissions due to vaporization from the spray nozzles and would therefore be expected to predict lower emission rates than would be measured. This was not the case, however. Due to the poor quality of the transect data, the measured data are perceived to have underestimated the true emission rate. However, it should be noted that both the predicted and measured emission rates had very broad confidence intervals, which both included the corresponding mean values and a zero emission rate. The imprecision of the predicted values is attributed to the wide variability in the concentrations of compounds found in the pond samples.

The Thibodeaux-Hwang air emission model was used to predict emissions from the landfarm. The predicted emissions show a time dependence, with the emission rate decreasing exponentially. The effect of retilling the area is

to increase emissions initially; however, the emission rate quickly returns to the range of values predicted if no tilling had occurred. The predicted emission rates were compared with the emission rates measured using the flux chamber and concentration-profile techniques. In general, the predicted emissions agreed with the measured emissions for specific compounds, but did not agree with the compound classes and total nonmethane hydrocarbon emission rates. In all cases, the predicted emission rates were significantly greater than the measured emission rates for the compound classes and total nonmethane hydrocarbons. This discrepancy may be caused, at least in part, by the composite parameters which were used for the compound classes. The Thibodeaux-Hwang model was developed for single components. To apply the model to multicomponent compound groups or classes, a set of parameters was developed for each group by averaging the parameter values of the more prominent compounds contained within the group. A more sophisticated approach may be needed to extend the model to multicomponent systems.

Existing predictive models were not used to estimate emissions from the inactive chemical landfills in light of the heterogeneous nature of the waste and inability of the existing models to account for vented emissions.

The API empirical model for breathing losses was used to predict breathing losses from four of the fixed-roof tanks at Site 6. The annual emission rates predicted by the API model were then used to calculate flow rates through the vents. Additionally, vent flow rates were calculated based upon vapor displacement calculations. The flow rates calculated by each method are quite similar, and all were at or below the detection limits for the flow measurement techniques used on site. The field observations and predicted emission rates from the fixed-roof tanks are therefore consistent with each other.

In summary, the Thibodeaux, Parker, and Heck surface impoundment model appears to be generally applicable to individual compounds in impoundments having no oil on the surface and/or no mechanical sprays. The Thibodeaux-Hwang landtreatment model appears to adequately describe the emissions of single compounds. However, it was not found to be satisfactory for compound classes or total NMHC emissions.

SECTION 3

DESCRIPTION OF SAMPLING SITES

Testing was performed at four separate HWDFs during this study. These sites were designated as Site 2, Site 4, Site 5, and Site 6. Brief descriptions of these facilities are provided below.

SITE 2

Site 2 is a commercial waste disposal operation which exclusively services four industrial clients. The site is located in the Gulf Coast area. Site 2 includes both a landfarm and a landfill. It has been in operation since 1980.

The landfarm is a single 4 hectares (10-acre) lot of land. The landfill consists of multiple cells with an overall dimension of 153m x 549m x 58m (500' x 1800' x 15') deep. Landfarmed wastes are predominantly petroleum refinery sludges, and are pumped on the surface of the landfarm and spread with a toothed harrow (teeth up). The oil content of the applied waste is estimated at 5-10%. The landfarm is tilled daily except during periods of bad weather. The soil is native clay.

The landfill contains four active cells, but only one was tested for emissions. The tested cell, Cell Q, contains solids from the following manufacturing processes: acrylonitrile, acetone cyanohydrin, lactic acid, tertiary butylamine, and iminodiacetic acid.

SITE 4

Site 4 is a commercial hazardous waste management facility located in the northeastern United States. The site covers 146 hectares (365 acres). A variety of hazardous and nonhazardous wastes are accepted at the facility. The site includes the following activities:

- wastewater treatment (WWT) including open tanks and lagoons,
- drum transfer and processing,
- active and inactive chemical landfills, and
- the sludge disposal facility.

Two sources, active chemical landfill area D and inactive chemical landfill area C, were tested for emissions.

Landfill D was opened in February of 1982 and will be closed in mid-1984. Liquid wastes are not accepted, and the waste material is currently limited to five percent free fluid, including air. Landfill D is divided

into five cells containing, respectively, heavty metals, flammable solids, general organics, heavy metals, and PCBs/pesticides. The dimensions of this landfill are 244m x 160m x 9m (800' x 525' x 28') deep at grade.

Landfill C is closed and contains gas vents as well as stand pipes for leachate collection. The stand pipes are open to the atmosphere. Gas vents are valved shut, with provisions for release through carbon canisters if gas pressure builds up within the cells. The final cover for Landfill C consists of 1m (3') of compacted clay, an 80 mil polyethylene liner, sand lens, 0.5m (18") clay, gravel and loam, and 0.2m (6") of topsoil.

SITE 5

Site 5 is a commercial hazardous waste management facility located in the northeastern United States. The site was developed for hazardous waste operations in the early 1970s. Activities at the site include:

- closed bulk storage tanks,
- drum storage in warehouses,
- chemical landfills (a total of 9),
- a recovery process for solvents and blending of fuels, and
- aqueous wastewater treatment.

The latter four activities were tested for emissions.

The total area of the site is 300 hectares (750 acres), with the facility proper occupying about 140 hectares (350 acres). The landfills accept pseudo metals, heavy metals, general organics, flammables, and toxics in both bulk and drums. These general waste categories are isolated within the landfill. Municipal waste is not co-disposed. Closed landfills include open gas vents, lysimeters, and a leachate collection system. Leachate is pumped to the wastewater treatment facility. The daily cover consists of 0.2m (6") of a clay/soil mix. The final cover consists of 1m (3') of compacted clay, a synthetic liner, 0.6m (2') of uncompacted clay, and 0.2m (6") of top soil/sod. Emissions were measured from active chemical landfill 10 and inactive chemical landfill 7.

The site's aqueous wastewater treatment (WWT) system has a throughput of 545,000 lpd (144,000 gdp) with typical discharges ranging from 330,000-382,000 lpd (86,400-100,800 gpd). Wastes accepted include wash waters, pickle liquors, and leachates from other facilities within the WWT. The WWT process at Site 5 includes chemical, physical, and biological treatment. The holding pond 6, reducing lagoon 1, and oxidizing lagoon 2 of the WWT system were tested for emissions.

SITE 6

Site 6 is a commercial chemical conversions and reclaiming facility located in the eastern United States. Solvents are recycled at the facility. The operations at the facility include:

- drum storage and transfer,
- truck transfer,
- the fractionating process area (thin film evaporator, batch evaporator and blending/washing vessel),
- storage tanks, and
- evaporation ponds.

Emissions from the storage tanks, fractioning process, and evaporation pond were measured at Site 6. The entire site encompasses approximately 4.2 hectares (10.5 acres), but the facility proper is confined to 1.9 hectares (4 3/4 acres). Pond 3 is 27m x 18m x 2m (90' x 60' x 7.5') and is an evaporation pond with four fog nozzles to promote evaporation. It receives rainfall, drainage, and process water from the site.

The fractionating process is closed to the atmosphere with the major waste product being still bottoms with small amounts of waste being produced from miscellaneous sources such as spills, etc. However, solvent washing and by-product collection are open to the atmosphere.

Storage tanks at Site 6 range in size from 1,300-32,000ℓ (338-8,400 gallons) for the storage of intermediates and products. A variety of waste materials are stored in tanks ranging from 26,500-71,800ℓ (7,000-18,961 gallons). Three underground storage tanks are used to store boiler fuel. Storage tanks are vented directly to the atmosphere.

SECTION 4

AIR EMISSION MEASUREMENTS

The sampling approaches for measuring air emissions from TSDFs included: 1) emission isolation flux chamber, 2) vent sampling, 3) concentration-profile, 4) transect technique, and 5) mass balance. These approaches can be classified as direct techniques (1 and 2) and indirect techniques (3, 4, and 5). These sampling approaches should be differentiated from the sampling and analytical techniques used to collect and/or analyze the samples. For the field sampling programs described here, air sample collection was by gas-tight syringe (on-site analysis) or evacuated stainless-steel canisters (off-site analysis). Sample analysis was performed on site using a field portable GC-FID (1 ppmv-C detection limit), and off site using a capillary column GC-FID/PID/HECD with cryogenic concentration and subambient temperature programming (1 ppbv-C detection limit).[7] Any liquid or solid samples were collected in glass containers, in a manner which would minimize any headspace. Analysis of the liquid and solid samples were performed using the GC-FID/PID/HECD. As a QC procedure, GC-MS analysis was performed on nominally 10 percent of the samples as confirmation of compound identification.

EMISSION ISOLATION FLUX CHAMBER

The emission isolation flux chamber is a device used to make a direct emission measurement. The enclosure approach has been used by researchers to measure emission fluxes of sulfur and volatile organic species.[8,9,10] The approach uses an enclosure device (flux chamber) to sample gaseous emissions from a defined surface area. Clean dry sweep air is added to the chamber at a fixed controlled rate. The volumetric flow rate of sweep air through the chamber is recorded and the concentration of the species of interest is measured at the exit of the chamber. The emission rate is expressed as:

$$E_i = C_i R/A \qquad \text{(Equation 1)}$$

where,

E_i = emission rate of component i, ug/m^2-sec
C_i = concentration of component i in the air flowing from the chamber, ug/m^3
R = flow rate of air through the chamber, m^3/sec
A = surface area enclosed by the chamber, m^2

All parameters in Equation 1 are measured directly.

A diagram of the flux chamber apparatus used for measuring emission rates is shown in Figure 1. The sampling equipment consists of a stainless steel/acrylic chamber with impeller, ultra high purity sweep air and rotameter for measuring flow into the chamber, and a sampling manifold for monitoring and/or collection of the specie(s) of interest. Concentrations of total hydrocarbons are monitored continuously in the chamber outlet gas stream using portable flame ionization detector (FID)- and/or photoionization detector (PID)-based analyzers. Samples are collected for subsequent gas chromatographic (GC) analysis once a steady-state emission rate is obtained. Air and soil/liquid temperatures are measured using a thermocouple.

To determine the emission rate for a source of much greater area than that isolated by the flux chamber, a sufficient number of measurements must be taken at different locations to provide statistical confidence limits for the mean emission rate. The area sources measured were gridded and a minimum of six (6) measurements made (when possible) to account for spatial variability. Additionally, a single point was selected as a control point to define temporal variability. On-site GC analyses were performed for all flux chamber measurements and several canister samples were collected for each area to allow off-site detailed GC analysis. Prior to using the chamber, blank and species recovery data were obtained.

VENT SAMPLING

Methods for measuring emissions from ducted sources are well documented.[11] The approach requires that the volumetric flow rate of the gas be determined, typically as measurements of velocity and duct cross-sectional area, and that the gas concentration be measured. The emission rate can then be calculated as:

$$E_i = C_i U A \qquad \text{(Equation 2)}$$

where,

E_i = emission rate of component i, ug/sec
U = gas velocity through vent, m/sec
C_i = concentration of component i in vent gas, ug/m^3
A = cross-sectional area of vent, m^2

All parameters in Equation 2 are measured directly.

CONCENTRATION-PROFILE

The concentration-profile (C-P) technique was developed by L. J. Thibodeaux and coworkers at the University of Arkansas under a U.S. Environmental Protection Agency contract.[12]. The C-P technique, as developed by Thibodeaux, has been used to measure emission rates of volatile species from wastewater treatment ponds,[12,13,14] and more recently from landtreatment facilities. The C-P approach is an indirect sampling technique predicated upon experimental measurements of wind velocity, volatile species concentration and temperature profiles in the boundary layer above the waste

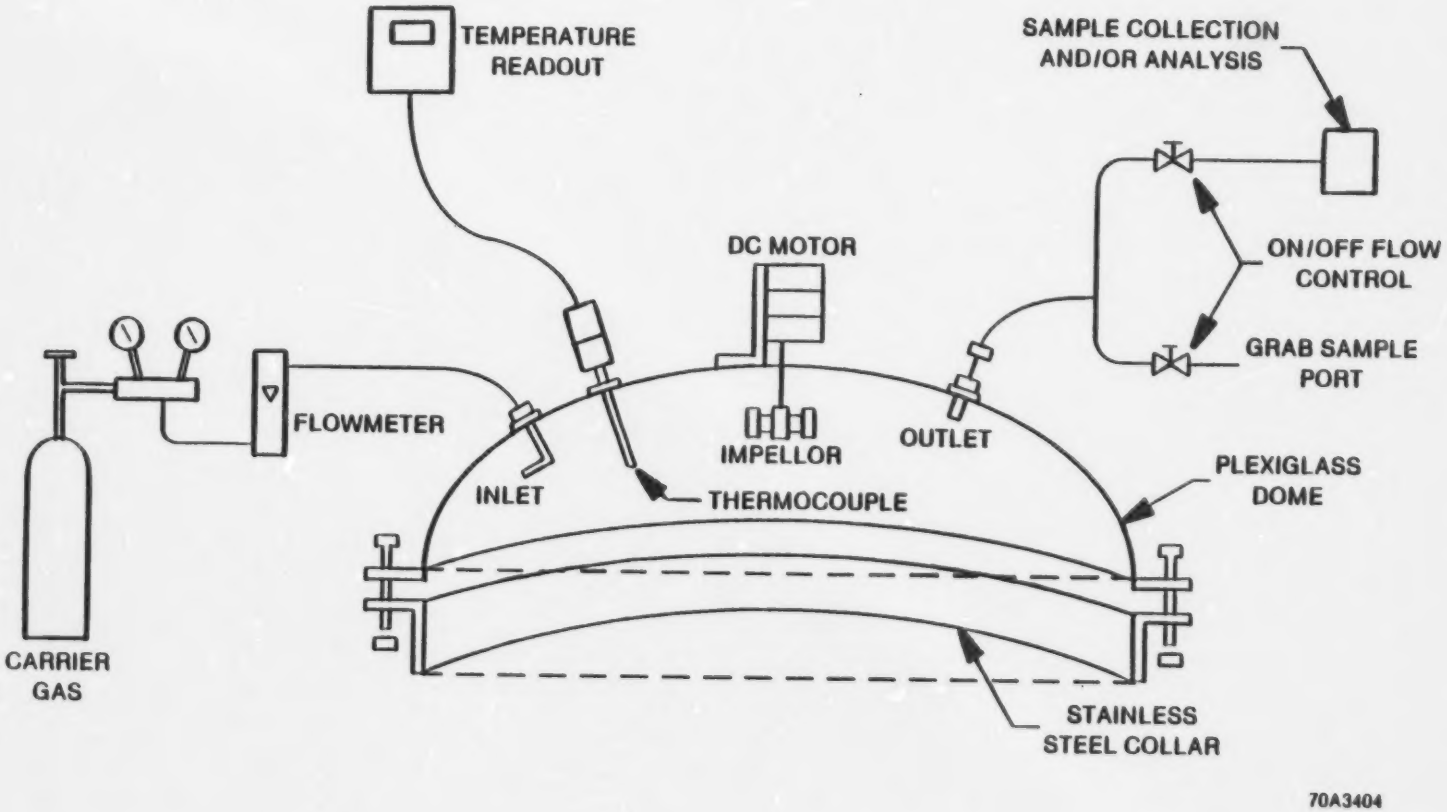

Figure 1. Cutaway side view of emission isolation flux chamber and sampling apparatus.

body. These measurements are used to estimate the vertical flux of the volatile species as:

$$E_i = \left(\frac{D_i}{D_{H_2O}}\right)^n S_v S_i K^2 / \phi_m{}^2 S_c \qquad \text{(Equation 3)}$$

where,

E_i = emission rates (flux) of organic species i, g/cm^2-sec
D_i = molecular diffusivity of organic species i in air, cm^2/sec
D_{H_2O} = molecular diffusivity of water vapor in air, cm^2/sec
K = von Karman's constant,
S_v = logarithmic slope of the air velocity profile, cm/sec
S_i = logarithmic slope of the concentration-profile for organic species i, g/cm^3
ϕ_m = Businger wind shear parameter
S_c = turbulent Schmidt number
n = exponent for diffusivity ratio

The term $(\phi_m{}^2 S_c)^{-1}$ represents an atmospheric stability correction factor and is expressed as a function of the Richardson number. The function is an empirical correlation which corrects the estimated emission rate for water vapor to measured values under various atmospheric stabilities. For this reason, the correction factor is valid only under specific meteorological conditions. The molecular diffusivities of water and many organic species are available in the open literature.[15,16] Diffusivities for those compounds for which values are not available, and compound classes or total hydrocarbons must be estimated.

A diagram of the C-P sampling system is shown in Figure 2. The sampling equipment consists of the following: a 4-meter mast with a wind direction indicator, wind speed sensors, temperature sensors, and air collection probes spaced at six logarithmic intervals; a continuous real-time data collection system; a thermocouple for measuring water temperature; and water sampling equipment.

Prior to sample collection, meteorological conditions were monitored for twenty (20) minutes to determine compliance with the necessary meteorological criteria, a canister blank was taken, and the air collection probes were purged. Once acceptable meteorological conditions were documented, a twenty (20) minute sample collection period was initiated. During the sample collection period, wind speed, air temperature, water temperature, and relative humidity were measured and water samples were obtained. Provisions were made for duplicate air samples to be taken from one of the air collection probes. An upwind air sample was also collected, although it is not expressly required by the methodology. A total of three C-P runs were performed for each of the area sources.

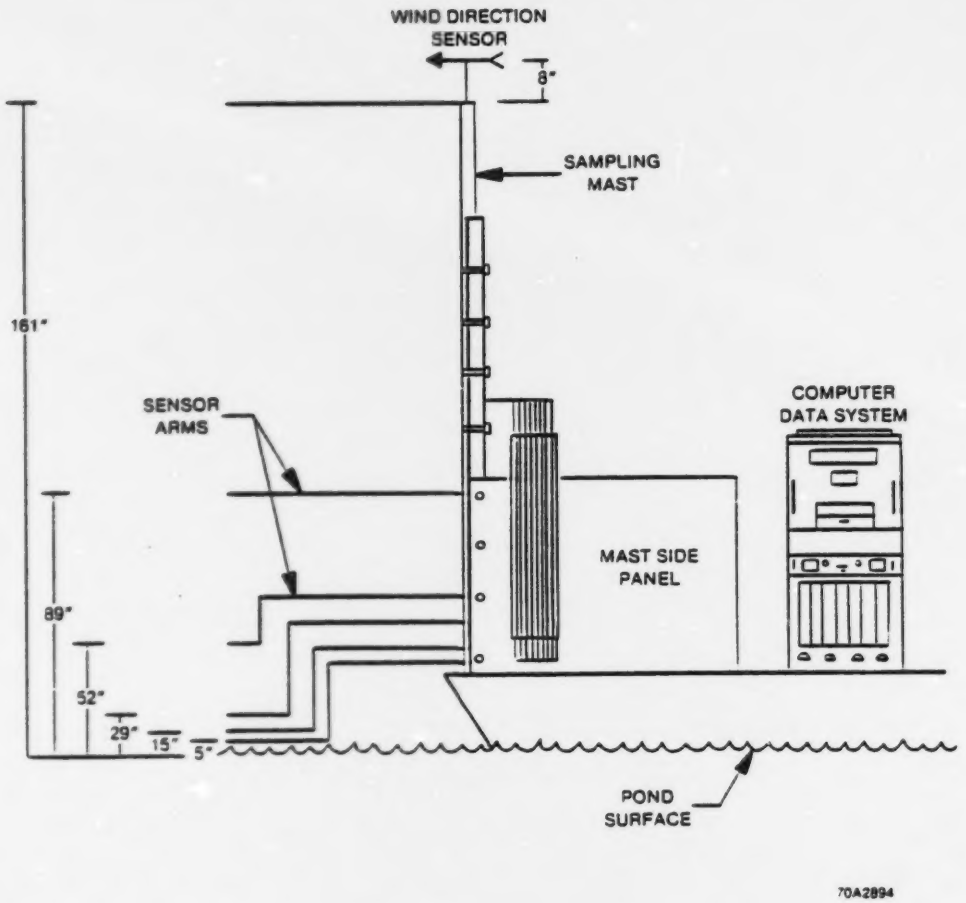

Figure 2. Mass sample collection system.

TRANSECT TECHNIQUE

The transect technique is an indirect emission measurement approach which has been used to measure fugitive particulate and gaseous emissions from area and line sources.[17,18] Horizontal and vertical arrays of samplers are used to measure concentrations of volatile specie(s) within the effective cross-section of the fugitive emission plume. A normal concentration distribution or curve is fitted to the measured concentrations. The volatile specie(s) emission rate is then obtained by spatial integration of the concentrations over this assumed plume area:

$$E_i = uA_s \iint_{A_p} C_{i(h,w)}\, dhdw \qquad \text{(Equation 4)}$$

where,

E_i = emission rate of component i, ug/m^3-sec
u = wind speed, m/sec
C_i = concentration of component i at point (h,w), corrected for upwind background, ug/m^3
h = vertical distance coordinate, m
w = horizontal distance coordinate, m
A_s = surface area of emitting source, m^2
A_p = effective cross-sectional area of plume, m^2

A diagram of the transect sampling system is shown in Figure 3. The sampling equipment consists of a central 3.5 meter mast having three equally spaced air sampling probes and single wind direction, wind speed, and temperature sensors at the top, and five 1.5 meter masts with single air sampling probes. The central mast is aligned with the expected plume centerline. Two masts are placed at equal spacings on each side of the central mast and one mast is used to collect air samples at an upwind location. The spacing of the associated masts are selected to cover the expected horizontal plume cross-section, as defined by oservation and/or profiling with a real-time total hydrocarbon (THC) analyzer.

Prior to sample collection, meteorological parameters were monitored for 20 minutes to determine if acceptable conditions existed, canister blanks were obtained, and the air sampling probes were purged. Following documentation of acceptable meteorological conditions, a 20-minute sampling period was initiated. During the sampling period, meteorological parameters were monitored. A total of three transect runs were made at each of the area sources.

MASS BALANCE

Theoretically, emissions or losses from any process can be estimated from an accurate mass balance. If all inlet and outlet process streams are precisely characterized with regard to flow rates, composition, and physical properties, any difference between the total known amount of material entering the system and that known to be leaving would be losses. This can be expressed as:

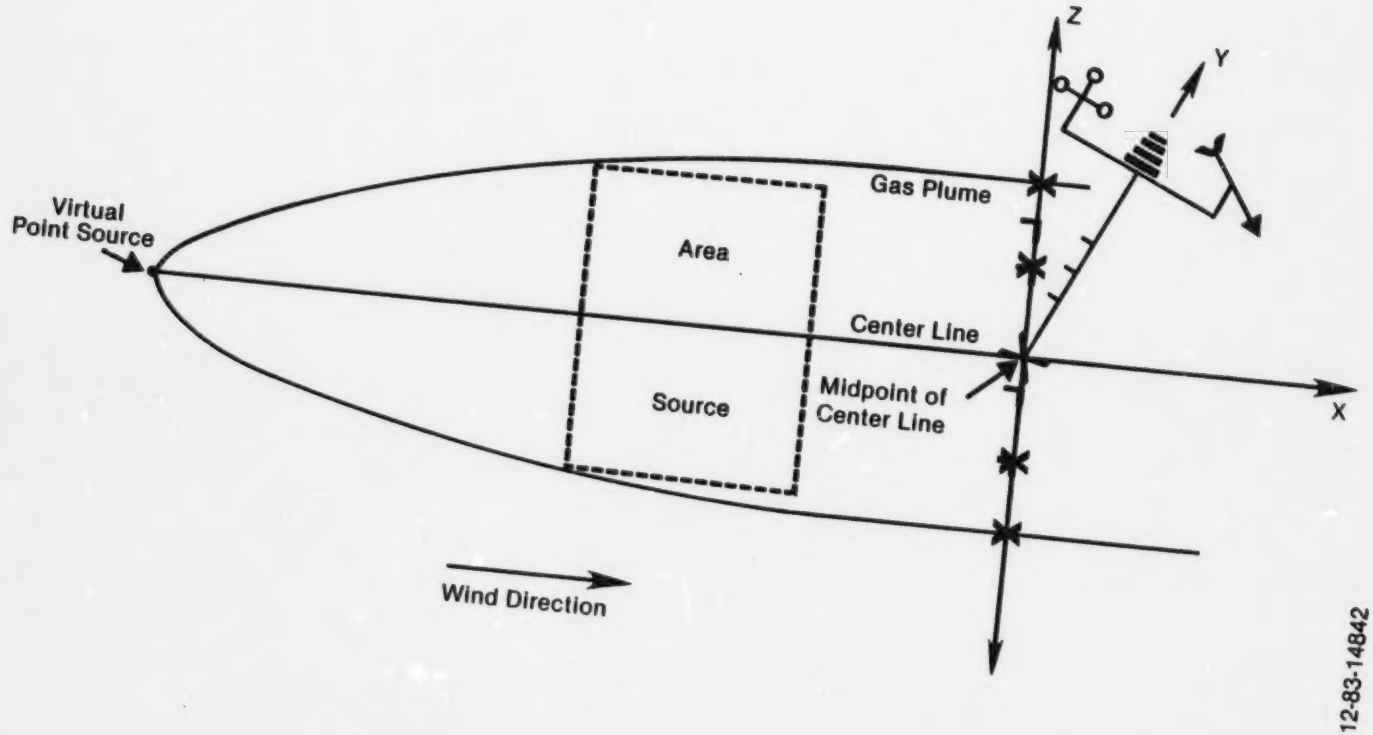

Figure 3. Example of transect technique sampling.

Mass Losses = Mass In - Mass Out (Equation 5)

In practice, precise measurements of material volumes, flow rates, and characteristics are often difficult to obtain. Most flow rates and material rate measurements in chemical processing are made in terms of volume. Thus, fluid densities must be known to convert volumetric measurements to mass flows. A liquid material balance can be expressed as:

$$E_i = \sum_j L_j W_{i,j} P_j - \sum_k L_k W_{i,k} P_k \qquad \text{(Equation 6)}$$

where,

E_i = emissions (losses) of component i, kg
L_j = volume of inlet stream j, m^3
L_k = volume of outlet stream k, m^3
$W_{i,j}$ = weight fraction of component i in inlet stream j
$W_{i,k}$ = weight fraction of component i in outlet stream k
P_j, P_k = density of liquid stream j and k, respectively, kg/m^3

All parameters in Equation 6 are measured. The emissions can also be expressed as a percentage of the total mass throughput of the process.

SECTION 5

PREDICTIVE AIR EMISSION MODELS

The predictive and mathematical models which have been proposed for describing the emission rates of volatile materials from source types present at HWDFs have been summarized in Table 1. In this study, the measured emission rates have been compared to the predicted emission rates from three types of sources; surface impoundments (non-aerated), landtreatment areas, and fixed roof storage tanks (breathing losses). The models which have been used to estimate emissions for comparative purposes in this study are described below.

SURFACE IMPOUNDMENT (NON-AERATED) MODEL

The Thibodeaux, Parker and Heck[12] model which is applicable to surface impoundments under steady-state conditions was used to predict emission rates from surface impoundments. This model (Table 5) is based on accepted theories of mass transfer. The basic assumption of this model is that of steady state, i.e., the concentrations of species of interest remain essentially constant in the aqueous phase. This implies a steady inlet rate and a steady biodegradation rate for each species of interest. In addition, an ideal solution is assumed, in which there are no interferences or interactions between species in the aqueous phase. Two individual mass transfer coefficients (k_l,k_g) must be determined when using the model. These are obtained from empirical relationships, some of which are relatively complex.

LANDTREATMENT MODEL

A mathematical model for predicting atmospheric emissions of volatile chemical compounds from landtreatment operations (including those of petroleum refineries) has been proposed by Thibodeaux and Hwang[19]. This model is presented in Table 6. In the development of this model, the emission rate of a volatile chemical compound is assumed to be a function of:

- the evaporation rate of the compound from the interstitial soil surfaces, and
- the diffusion rate of the chemical compound through the air-filled pore spaces of the soil.

The emission rate is assumed to be controlled by the diffusion rate in the air pore space when the oil loading and soil particles are both small.

The Thibodeaux-Hwang model, as developed, applies strictly to single chemical compounds. The emissions of groups or classes of compounds have

TABLE 5. THIBODEAUX, PARKER, AND HECK EMISSION MODEL FOR AERATED AND/OR UNAERATED SURFACE IMPOUNDMENT

Model: Thibodeaux, Parker, and Heck (12)

Disposal Method: Surface Impoundment

Type of Model: Predictive

Basis: Mass transport theory concepts, with individual mass transfer coefficients obtained through the two resistance theory

Form:

$$q_i = M_i K_{li} (X_i - X_i^*)$$

and, for each volatile component i

$$K_l = (K_l^t A_t + K_l^n A_n)/(A_t + A_n)$$

$$\frac{1}{K^t} = \frac{1}{k^t} + \frac{1}{Hk_g^t}$$

$$\frac{1}{K_l^n} = \frac{1}{k_l^n} + \frac{1}{Hk_g^n}$$

Symbol	Symbol/Parameter Definition	Source of Input Parameters
q_i	Flux of component i from the impoundment surface, g/cm^2-s	-
M_i	Molecular weight of component i, g/g-mol	Published data
K_{li}	Overall liquid-phase mass transfer coefficient for component i, mol/cm^2-s	Calculation
X_i	Mole fraction of component i in the aqueous phase	Measured
X_i^*	Mole fraction of component i in equilibrium with the mole fraction of component i in the air, y_i. If y_i is assumed to be negligibly small, $X_i^* = 0$.	Calculated from measured concentrations in the atmosphere
K_l^t, K_l^n	Overall liquid-phase mass transfer coefficients for the turbulent (aerated) and natural (unaerated) zones of the impoundment, respectively, mol/cm^2-s	Calculated

(Continued)

TABLE 5. (Continued)

Symbol	Symbol/Parameter Definition	Source of Input Parameters
A_t, A_n	Surface areas of the turbulent and natural zones, respectively, cm	Measured
k_l^t, k_l^n	Individual liquid phase mass transfer coefficients for the turbulent and natural zones, respectively, mol/cm -s	Calculated from empirical correlations*
k_g^t, k_g^n	Individual gas phase mass transfer coefficients for the turbulent and natural zones, respectively, mol/cm -s	Calculated from empirical correlations*
H	Henry's law constant in mole fraction form, $y = Hx$	Published data or estimation

*Empirical Correlation for Individual Mass Transfer Coefficients are shown below.

$$k_l^t \quad \frac{0.823\ J\ (POWR)\alpha(1.024)^{\theta-20}}{a_v V -} \frac{D_{iw}}{D_{a_2 w}} \qquad (a)$$

$$k_g^t \quad 1.35\times10^{-5} \frac{\rho g\ D_{iA}}{d} N_{Re}^{1.42} N_p^{0.40} N_{Sc}^{0.5} N_{Fr}^{-0.21} \qquad (b)$$

N_{Re} Reynolds Number, $d^2 w\ \rho g/Mg$

N_p Power Number, $P_r g_c/\rho l\ d^3 w^3$

N_{Sc} Schmidt Number, $Mg/D_{i,air}\ \rho g$

N_{Fr} Froude Number, dw^2/gc

$$k_l^n \quad 4.24\times10^{-4}\ (1.024)^{\theta-20}\ U_o^{0.67}\ H_o^{-0.85} \left(\frac{D_{iw}}{D_{o_2 w}}\right) \qquad (c)$$

$$k_g^n \quad 1.30\times10^{-5}\ U_{air}^{0.78}\ N_{Sc}^{-0.67}\ d_e^{-0.11} \frac{\rho g}{MW_{air}} \qquad (d)$$

(Continued)

TABLE 5. (Continued)

Notation for Variables in Empirical Correlations

J	Oxygen-transfer rating of surface aerator, normally in the range of about 2-4 lb O^2/hr-hp
POWR	total power input to aerators in aerated surface impoundment, Hp
α	correction factor for wastewater/clean water oxygen transfer (0.80 to 0.85)
θ	water temperature, °C
D_{iw}	diffusion coefficient for component i in water, cm^2/sec
$D_{o\ w}$	diffusion coefficient for oxygen in water, cm^2/sec
a_v	surface area per unit of volume of surface impoundment, ft^{-1}
V	volume of surface impoundment in region affected by aeration, ft^3
ρg	density of air, lb/ft^3 (gr/cm in Eq. b)
$D_{i,air}$	diffusion coefficient for component i in air, cm^2/sec
d	diameter of aerator turbine or impeller, ft (cm in Eq. b)
w	rotational speed of turbine impeller, rad/sec
Mg	viscosity of air, g/cm-sec
pr	power to impeller, ft-lb force/sec
gc	gravitational constant, 32.2 ft/sec^2
e	density of liquid, lb/ft^3
U_o	surface velocity, ft/sec
H_o	effective depth of surface impoundment, ft
U_{air}	wind speed, m/hr
d_e	effective diameter of quiescent area of surface impoundment, m
MW_{air}	molecular weight of air, lb/lb-mole

TABLE 6. DESCRIPTION OF THIBODEAUX-HWANG LANDTREATMENT AIR EMISSION MODEL

Model: Thibodeaux-Hwang

Disposal Method: Landtreatment

Type of Model: Predictive

Basis: Emission rate is controlled by diffusion of vapor through the air-filled pores of the landtreated soil.

Form:

$$q_i = \frac{D_{ei}\ C_{ig}}{\left[h_s^2 + \frac{2\ D_{ei}\ t\ A\ (h_p - h_s) C_{ig}}{M_{io}}\right]^{1/2}}$$

and

$$C_{ig} = \left[\frac{H_c}{1 + H_c\ \frac{D_{ei}\ Z_o}{D_{wi}\ A_s\ f(\bar{y})}}\right] C_{io}$$

Symbol	Symbol/Parameter Definition	Source of Input Parameter
q_i	flux of component i from the soil surface, g/cm^2-sec	
D_{ei}	effective diffusivity of component i in the air-filled soil pore spaces, cm^2/s	published data estimation
C_{ig}	effective wet zone pore space concentration of component i, g/cm^3	calculated
h_s	depth of subsurface injection (if applicable), cm	measured
h_p	depth of soil contaminated or wetted with land-treated waste, cm	measured
t	time after application, sec	measured
A	surface area over which waste is applied, cm^2	measured
M_{io}	initial mass of component i incorporated into the zone $(h_p - h_s)$, g	measured

(Continued)

TABLE 6. (Continued)

Symbol	Symbol/Parameter Definition	Source of Input Parameter
H_c	Henry's-law constant in concentration form, cm^3 oil/cm^3 air	published data or measurement
Z_o	oil layer diffusion length, cm	calculated or estimated
D_{wi}	effective diffusivity of species i in the oil, cm^2/s	published data estimation
A_s	interfacial area per unit volume of soil for the oily waste, cm^2/cm^3	calculated
$f(\bar{y})$	$y\ (h_p-\bar{y})$, accounts for the lengthening dry zone	calculated
$\bar{y}$	height of wetted soil remaining after partial drying, cm	measured

been estimated in this study, however, by assuming a single set of component properties for the entire class.

STORAGE TANK MODELS

Atmospheric emissions of volatile organic compounds from fixed roof tanks are of two types: breathing losses and working losses. Breathing losses occur as a result of vapor expansion within the tank due to changes in the tank vapor temperature and ambient barometric pressure. Breathing losses occur in the absence of any significant change of liquid level in the tank.

Working losses on the other hand are caused by vapor being expelled or drawn into the tank as a result of periodic filling and drawing down.

The tanks which were tested for emissions during the source tests were not subjected to any filling or emptying while the testing was being performed. Thus, only the breathing loss equation proposed by API[20] was applicable to predicting emission rates at the time of testing. This equation is presented in Table 7.

TABLE 7. EMISSION LOSSES FROM FIXED-ROOF TANKS - BREATHING LOSSES

Model: API Empirical Model

Disposal Method/ Source: Storage of Liquid Waste

Type of Model: Predictive

Basis: Empirical Correlation of Field Test Data

Form:

$$L_B = 2.21 \times 10^{-4} M \left[\frac{P}{14.7 + P}\right]^{0.68} D^{1.73} H^{0.51} \Delta T^{0.50} F_p C K_c$$

Symbol	Symbol/Parameter Definition	Source of Input Parameter
L_B	Fixed-roof breathing loss, lb/day	-
M	Molecular weight of vapor in storage tank, lb/lb-mole	Published data, measurement
P	True vapor pressure at bulk liquid conditions, psia	Published data or measurement
D	Tank diameter, ft	Specified, measured
H	Average vapor space height, including roof volume correction, ft; see note (1)	Calculated
ΔT	Average ambient temperature change from day to night, °F	Measured
F_p	Paint factor, dimensionless (range=1.00-1.58)	Tabulated values
C	Adjustment factor for small diameter tanks, see Figure 3-1	Correlation
K_c	Crude oil factor, dimensionless, see note (2)	Correlation

Note: (1) The vapor space in a cone roof is equivalent in volume to a cylinder which has the same base diameter as the cone and is one-third the height of the cone.

(2) K_c = (0.65) for crude oil, K_c = (1.0) for gasoline and all other liquids.

SECTION 6

MEASURED AND PREDICTED EMISSION RATES FROM HWDF SOURCES

A summary of the measured and predicted emission rates of some selected organic compounds and groups of compounds from sources at tested HWDFs is presented in this section of the report. Emission rates were measured from:

- surface impoundments,
- landtreatment areas,
- landfills/landfill vents,
- storage tanks,
- a drum storage area, and
- a solvent recovery process.

A variety of sampling approaches were used in the testing (see Section 4). Emission rates were also calculated for surface impoundments, landtreatment areas, and fixed roof storage tanks using predictive mathematical models (see Section 5). In the following discussions, the measured and predicted emission rates of selected compounds and groups of compounds are presented, and measured rates are compared with calculated rates. The variability associated with these sampling approaches and models was estimated and is discussed in Section 7, Data Quality.

SURFACE IMPOUNDMENTS

VOC emission rates were measured using direct and/or indirect methods from the following surface impoundments:

- Site 5 - Reducing Lagoon 1
  Oxidizing Lagoon 2
  Holding Pond 6
- Site 6 - Evaporation Pond 3

The rates were measured using the concentration-profile method, the transect technique, and the emission isolation flux chamber. Emission rates of individual and classes of compounds were estimated using the predictive model of Thibodeaux, Parker, and Heck[19]. Thus, the predicted rates can be compared with the emission rates actually measured for those compounds and/or classes.

Measured Emission Rates

The results of the emission rate measurements and predictions for the tested impoundments are summarized in Tables 8 through 12. Generally, emission rates were measured at several grid points on a source surface when

TABLE 8. MEASURED AND PREDICTED EMISSION RATES OF TOTAL NMHC FROM SURFACE IMPOUNDMENTS

Source	Measurement Method[a]	Total NMHC Emission Rate, kg-C/hectare-hr		Comments
		Measured	Predicted	
Reducing Lagoon 1: Site 5	FC	0.329 (0.162, 0.529)[b]	1.27 (0.0003, 2.79)	Measured at Grid Point 2
		0.522 (0.220, 0.846)	1.18 (0.0002, 2.75)	Measured at Grid Point 8
Oxidizing Lagoon 2: Site 5	FC	2.16 (1.07, 3.52)	612 (0.0004, 1745)	Measured at Grid Point 1
		1.96 (0.831, 3.11)	183 (0.0004, 522)	Measured at Grid Point 7
Holding Pond 6	CP	0.0066 (-0.03, 0.046)	0.680 (0.0004, 1.42)	CP Run Number 1
	CP	0.0752 (-0.061, 0.241)	0.713 (0.0608, 1.52)	CP Run Number 2
	CP	0.0201 (-0.006, 0.0633)	0.810 (0.0004, 1.74)	CP Run Number 3
	FC	0.0950 (0.0371, 0.153)	0.713 (0.0608, 1.52)	Corresponds to CP Run Number 2
	FC	0.139 (0.0543, 0.215)	0.810 (0.0004, 1.74)	Corresponds to CP Run Number 3
Evaporation Pond 3: Site 6	T	1.98[c] (0.526, 6.19)	7.09[d] (0.0004, 14.4)	Transect Run Number 1
	T	1.50[c] (0.439, 5.80)	7.09[d] (0.752, 14.6)	Transect Run Number 2

[a]Measurement method code: FC = flux chamber, CP = concentration profile, T = transect
[b]Values in parentheses are lower and upper limits of the 95 percent confidence interval about the mean
[c]Losses by surface evaporation and spray nozzles
[d]Losses by surface evaporation only, the predicted model does not account for spray nozzles

TABLE 9. MEASURED AND PREDICTED EMISSION RATES OF VOLATILE ORGANIC COMPOUNDS FROM REDUCING LAGOON 1: SITE 5

Compound Class	Measurement Method	Emission Rate, kg-C/hectare-hr		Comments
		Measured	Predicted	
Olefins	FC	0.011 (0.005, 0.019)	0.052 (0.006, 0.113)	Measured at Grid Point 2
	FC	0.017 (0.008, 0.028)	0.033 (0.0003, 0.077)	Measured at Grid Point 8
Paraffins	FC	0.036 (0.014, 0.058)	0.053 (0.003, 0.121)	Measured at Grid Point 2
	FC	0.051 (0.023, 0.087)	0.058 (0.0002, 0.132)	Measured at Grid Point 8
Total Aromatics	FC	0.126 (0.054, 0.213)	0.522 (0.035, 1.13)	Measured at Grid Point 2
	FC	0.238 (0.108, 0.396)	0.432 (0.003, 0.878)	Measured at Grid Point 8
Total Halogenated HC	FC	0.154 (0.063, 0.249)	0.601 (0.012, 1.59)	Measured at Grid Point 2
	FC	0.195 (0.073, 0.334)	0.630 (0.054, 1.41)	Measured at Grid Point 8
Total NMHC	FC	0.329 (0.162, 0.529)	1.27 (0.0003, 2.79)	Measured at Grid Point 2
	FC	0.522 (0.220, 0.846)	1.18 (0.0003, 2.75)	Measured at Grid Point 8

TABLE 10. MEASURED AND PREDICTED EMISSION RATES OF VOLATILE ORGANIC COMPOUNDS FROM OXIDIZING LAGOON 2: SITE 5

Compound Class	Measurement Method	Emission Rate, kg-C/hectare-hr		Comments
		Measured	Predicted	
Olefins	FC	ND	47.9 (0.0009, 127)	Measured at Grid Point 1
	FC	ND	2.73 (0.0004, 7.20)	Measured at Grid Point 7
Paraffins	FC	0.226 (0.091, 0.374)	74.9 (0.0004, 199)	Measured at Grid Point 1
	FC	0.242 (0.102, 0.403)	99.7 (0.0004, 256)	Measured at Grid Point 7
Total Aromatics	FC	0.670 (0.301, 1.08)	284 (0.0003, 677)	Measured at Grid Point 1
	FC	0.267 (0.119, 0.443)	31.3 (2.16, 79.2)	Measured at Grid Point 7
Total Halogenated HC	FC	1.23 (0.580, 1.96)	170 (0.0005, 432)	Measured at Grid Point 1
	FC	1.45 (0.605, 2.45)	31.7 (0.0005, 89.6)	Measured at Grid Point 7
Total NMHC	FC	2.16 (1.07, 3.52)	612 (0.0005, 1750)	Measured at Grid Point 1
	FC	1.97 (0.832, 3.11)	183 (0.0005, 522)	Measured at Grid Point 7

ND = not detected

TABLE 11. MEASURED AND PREDICTED EMISSION RATES OF SELECTED ORGANIC COMPOUNDS FROM HOLDING POND 6, SITE 5

Compound or Compound Class	Measurement Method	Emission Rate, kg-C/hectare-hr		Comments
		Measured	Predicted	
3 Methylpentane	CP	0.0010(-0.0011,0.0031)	0.0058(0.0007,0.0115)	CP Run 1
	CP	0.0010(-0.0007,0.0033)	0.0036(0.0004,0.0078)	CP Run 2
	CP	0.0005(-0.0006,0.0018)	0.0006(0.0004,0.0013)	CP Run 3
	FC	0.0003(0.0001,0.0005)	0.0036(0.0004,0.0078)	Corresponds to CP Run 2
	FC	0.0003(0.0001,0.0005)	0.0006(0.0004,0.0013)	Corresponds to CP Run 3
Isobutene + 1-Butene	CP	-0.0006(-0.0012,-0.0001)	0.0123(0.0013,0.0267)	CP Run 1
	CP	0.0009(-0.0006,0.0026)	0.0097(0.0004,0.0206)	CP Run 2
	CP	-0.0001(-0.0005,0.0004)	0.0070(0.0004,0.0148)	CP Run 3
	FC	0.0008(0.0003,0.0013)	0.0097(0.0004,0.0206)	Corresponds to CP Run 2
	FC	0.0016(0.0006,0.0025)	0.0070(0.0004,0.0148)	Corresponds to CP Run 3
p-, m-Xylene	CP	0.0006(-0.0002,0.0012)	0.0526(0.0046,0.111)	CP Run 1
	CP	0.0017(0.0005,0.0036)	0.0619(0.0003,0.116)	CP Run 2
	CP	0.0007(0.0001,0.0017)	0.0637(0.0004,0.130)	CP Run 3
	FC	0.0086(0.0036,0.0148)	0.0619(0.0003,0.116)	Corresponds to CP Run 2
	FC	0.0110(0.0053,0.0180)	0.0637(0.0004,0.130)	Corresponds to CP Run 3
Toluene	CP	0.0029(0.0013,0.0050)	0.124(0.0035,0.279)	CP Run 1
	CP	0.0032(0.0014,0.0057)	0.139(0.0003,0.283)	CP Run 2
	CP	0.0029(0.0011,0.0056)	0.144(0.0153,0.294)	CP Run 3
	FC	0.0195(0.0080,0.0329)	0.139(0.0003,0.283)	Corresponds to CP Run 2
	FC	0.0180(0.0072,0.0298)	0.144(0.0153,0.294)	Corresponds to CP Run 3
Trichloroethylene + Bromodichloro-methane	CP	0.0009(0.0006,0.0014)	0.0976(0.0003,0.198)	CP Run 1
	CP	0.0010(0.0006,0.0014)	0.0623(0.0003,0.136)	CP Run 2
	CP	0.0009(0.0004,0.0017)	0.0688(0.0003,0.136)	CP Run 3
	FC	0.0108(0.0040,0.0177)	0.0623(0.0003,0.136)	Corresponds to CP Run 2
	FC	0.0128(0.0053,0.0198)	0.0688(0.0003,0.149)	Corresponds to CP Run 3

(Continued)

TABLE 11. (Continued)

Compound or Compound Class	Measurement Method	Emission Rate, kg-C/hectare-hr		Comments
		Measured	Predicted	
Paraffins	CP	0.0026 (-0.0108,0.0180)	0.0389(0.0004,0.0835)	CP Run 1
	CP	0.0194(-0.0105,0.0554)	0.0396(0.0004,0.0857)	CP Run 2
	CP	0.0102(-0.0008,0.0244)	0.0814(0.0004,0.168)	CP Run 3
	FC	0.0306(0.0014,0.0530)	0.0396(0.0004,0.0857)	Corresponds to CP Run 2
	FC	0.0042(0.0019,0.0067)	0.0814(0.0004,0.168)	Corresponds to CP Run 3
Total Aromatics	CP	0.0058(-0.0056,0.0199)	0.258(0.0003,0.536)	CP Run 1
	CP	0.0112(-0.0004,0.0252)	0.302(0.0003,0.648)	CP Run 2
	CP	0.0044(-0.0049,0.0143)	0.316(0.0003,0.706)	CP Run 3
	FC	0.0439(0.0201,0.0702)	0.302(0.0003,0.648)	Corresponds to CP Run 2
	FC	0.0547(0.0269,0.0972)	0.316(0.0003,0.706)	Corresponds to CP Run 3
Total Halogenated HC	CP	0.0022(-0.0113,0.0129)	0.298(0.0003,0.601)	CP Run 1
	CP	0.0358(-0.0508,0.124)	0.268(0.0003,0.536)	CP Run 2
	CP	0.0065(0.0013,0.0157)	0.298(0.0003,0.594)	CP Run 3
	FC	0.0396(0.0216,0.0608)	0.268(0.0003,0.536)	Corresponds to CP Run 2
	FC	0.0619(0.0274,0.0986)	0.298(0.0003,0.594)	Corresponds to CP Run 3
Total NMHC	CP	0.0066(-0.0296,0.0457)	0.680(0.0004,1.42)	CP Run 1
	CP	0.0752(-0.0608,0.241)	0.713(0.0608,1.52)	CP Run 2
	CP	0.0201(-0.0061,0.0634)	0.810(0.0004,1.74)	CP Run 3
	FC	0.0950(0.0371,0.153)	0.713(0.0608,1.52)	Corresponds to CP Run 2
	FC	0.134(0.0544,0.215)	0.810(0.0004,1.74)	Corresponds to CP Run 3

TABLE 12. MEASURED AND PREDICTED EMISSION RATES OF SELECTED ORGANIC COMPOUNDS FROM SPRAY EVAPORATION POND (POND 3): SITE 6

Compound or Compound Class	Measurement Method	Emission Rate, kg-C/hectare-hr		Predicted	Comments
		Method 1[a]	Method 2[b]		
Toluene	T	0.592 (0.180, 2.38)	0.662 (0.360, 9.79)	0.720 (0.0868, 1.46)	Transect Run 1
	T	NC	NC	0.709 (0.0143, 1.53)	Transect Run 2
1,1,1-Trichloro-ethane	T	NC	NC	1.80 (0.0003, 3.67)	Transect Run 1
	T	0.407 (0.127, 1.04)	0.551 (0.348, 1.23)	1.79 (0.172, 3.82)	Transect Run 2
Paraffins	T	0.652 (0.192, 3.05)	0.767 (0.443, 32.3)	0.450 (0.0004, 0.954)	Transect Run 1
	T	NC	NC	0.450 (0.0004,0.954)	Transect Run 2
Total Aromatics	T	0.986 (0.336, 4.39)	1.15 (0.724, 18.4)	1.16 (0.0997, 2.42)	Transect Run 1
	T	NC	NC	1.14 (0.0003, 2.11)	Transect run 2
Total Halogenated HC	T	0.161 (0.0317, 0.308)	0.209 (0.141, 0.306)	4.75 (0.0333, 9.72)	Transect Run 1
	T	0.472 (0.175, 1.47)	0.651 (0.418, 2.33)	4.72 (0.130, 10.7)	Transect Run 2
Total NMHC	T	1.98 (0.526, 6.19)	2.24 (1.35, 19.5)	7.09 (0.0004, 14.4)	Transect Run 1
	T	1.50 (0.439, 5.80)	2.16 (1.15, 7.60)	7.09 (0.752, 14.6)	Transect Run 2

[a]based on integration of the concentrations across the cross-section of the plume

[b]use of a dispersion model to estimate source strength which would result in the downwind concentrations

NC = emission rate could not be calculated because the data did not approximate a normal distribution

using the flux chamber. Detailed analytical data were typically obtained for several of these grid points. In the case of Holding Pond 6, however, emissions were measured at only one point, but concurrently with two of the concentration-profile test runs (Nos. 2 and 3). In general, the emission rates measured at different grid points on the impoundment surfaces are in quite good agreement (coefficient of variation less than 30%).

As summarized in Table 8, oxidizing Lagoon 2 (Table 10) had substantially higher emission rates as measured with the flux chamber than did similarly measured rates at Reducing Lagoon 1 (Table 9) and Holding Pond 6 (Table 11). The higher emission rates may be at least partially due to the presence of solids and liquid oil which were observed on the surface of Oxidizing Lagoon 2 in the areas where sampling was performed.

In addition to being directly measured with the flux chamber, the emission rates of VOC from Holding Pond 6 were also measured with the concentration-profile method. The measured emission rates of selected individual and classes of organic compounds are included in Table 11. Three separate test runs were performed to collect concentration-profile data at Holding Pond 6. The concentration-profile method requires that the slope of several profiles be determined. These profiles include:

- temperature as a function of height (above lagoon surface),
- wind speed as a function of height,
- wind speed as a function of the log of height,
- concentration as a function of the log of height.

Ideally, these profiles should be linear with clearly defined slopes. Most of the experimentally determined profiles were not linear, however, and the data were quite scattered, particularly in the case of the temperature profile. This is not surprising, because the total temperature range was less than 0.5°C.

It can be seen in Table 11 that the estimated emission rates of the selected individual compounds are quite consistent among the three runs. The estimated emission rates of the classes of compounds do vary considerably, however, from run to run. One possible cause of some of the variation might be the necessary use of one set of generalized properties for each class of compounds. The width of the 95 percent confidence interval is generally greater, for the compound classes than for the individual components. Thus, within each test run, the estimated emission rates of the selected individual compounds appear to be more precise than those of the compound classes.

In general, the emission rates estimated with the concentration-profile method are lower than those measured with the flux chamber. The flux chamber does isolate the measured source area from the wind. The rate measured with the flux chamber might be expected to be lower, if anything, than the emission rates measured from the exposed source (concentration-profile method). It appears, then, that the emission rate estimated by the concentration-profile method for Holding Pond 6 may be somewhat low. Both the

individual and overall variability of the measured emission rates (as computed from Monte Carlo simulations) are greater for the concentration-profile method (CVs > 100%) than for the flux chamber method (CVs ≈ 30%).

The transect technique was used in estimating the emissions of VOC from Spray Evaporation Pond 3 at Site 6. Emission rate estimation by the transect method requires that the maximum component concentrations, as well as the standard deviations in the horizontal and vertical directions, be determined. This is accomplished by fitting normal curves to the concentration test data. The transect concentration data for the selected compounds were widely scattered. For many of the compounds, a normal curve could not be realistically fitted to the data. Even in those cases where the normal curves could best be fitted, the actual concentration data points adhered only poorly to the fitted curves.

The emission rates estimated by the transect technique at the spray evaporation pond are summarized in Table 12. The emission rates were estimated using two slightly different procedures (designated as Method 1 and Method 2). Method 1 is a direct integration of the concentration across the entire cross-section of the plume. Method 2 involves the use of the downwind dispersion model to estimate emission rates. The emission rates calculated by Method 2 appear to be consistently higher than those calculated by Method 1. The magnitude of the differences between the mean rates calculated by both methods is relatively small, in the range of 20-50%. However, the 95 percent confidence intervals are quite broad, reflecting the considerable degree of scatter in the concentration-profile data. The 95 percent confidence intervals overlap the mean emission rates calculated for each component or compound class. Furthermore, it is not yet possible to tell which of the two calculational methods provides the most accurate emission rate estimate.

Both the concentration-profile and transect measurement techniques are very sensitive to ambient weather conditions (primarily windspeed and direction) and localized physical parameters. During this program, there were frequent incidences when scheduled emission data could not be obtained because of unsatisfactory meteorological conditions, physical configurations at the sampling site, or both. In other cases, data were collected under borderline meteorological conditions because satisfactory conditions were not present and/or could not be achieved during the scheduled on-site test period.

Predicted Emission Rates

Water samples were collected at each of the surface impoundments that were tested for emissions. These samples were generally taken at the same time, and in the case of flux chamber sampling, at the same grid points where emissions were directly measured. The concentration of the various organic compounds in the water samples was determined. These concentrations were used in the Thibodeaux, Parker, and Heck model to predict emission rates from the various impoundments. The predicted emission rates are included in Tables 8 through 12.

The predicted emission rates of classes of compounds are shown in Table 8 for two grid points on Reducing Lagoon 1 (Site 5). The differences in emission rates between grid points are relatively small, and the precision of the individual calculated emission rates is quite good.

On the other hand, as seen in Table 10, the predicted emission rates of the major compound classes from Oxidizing Lagoon 2 (Site 5) are substantially different at the two sampled grid points. Extremely high emissions were predicted in comparison with the magnitude of predicted emission rates from other impoundments. The apparent cause of these differences was the nature of the lagoon surface at the point where liquid samples were collected. Grid 7 appeared to have a considerable amount of sludge on the surface, while oil was present in Grid 1. The liquid (or sludge) samples taken at these locations had very high concentrations of organic compounds, (30-100% NMHC) as might be expected in an organic sludge or oil layer. Since the hydrocarbon content of the samples was so high, the hydrocarbon vapor-liquid equilibrium constants were used instead of Henry's law constants in the predictive equation. The emission rates predicted using the vapor-liquid equilibrium constants are 2-4 orders of magnitude less than those predicted with Henry's law constants.

The precision of the rates calculated at the individual grid points on Oxidizing Lagoon 2 appears to be of the same relative magnitude as the majority of other predicted rates. The emission rates predicted at the two grid points should not be extrapolated to the entire area of Oxidizing Lagoon 2, because most of the surface was not covered with a separate hydrocarbon layer. When differences exist in the composition of the impoundment, multiple samples are required. The average emission rate can then be estimated by weighting the values according to surface area.

Liquid samples were collected during the concentration-profile and flux chamber testing at Holding Pond 6 (Site 5). The samples taken during CP Run 3 contained substantially lower levels of organic compounds compared to the levels in the CP Run 1 and 2. As shown in Table 11, the emission rates predicted for CP Run 3 were consequently much lower than those predicted during CP Runs 1 and 2. However, the measured rates did not evidence any substantially lower values during CP Run 3 compared to the rates measured for Runs 1 and 2. All of the predicted emission rates were relatively low, however. The precision of the emission rates calculated for CP Run 3 is also poorer than that of CP Runs 1 and 2. The precision of emission rate predictions for these latter runs was about the same general magnitude as those predicted for Reducing Lagoon 1 and Oxidizing Lagoon 2.

The Spray Evaporation Pond 3 at Site 6 contained four fog nozzles that were in operation at the time of the transect sampling. The Thibodeaux Parker, Heck surface impoundment air emission model applies only to vaporization occurring at the liquid surface. It does not consider vaporization due to the spray nozzles.

Samples of the water in the spray evaporation pond were collected during the two transect testing periods (which occurred in close sequence).

The results of the liquid analyses were used to define average compositions for the aqueous phase. Since these average concentrations were used in the predictive equation, the predicted emission rates of each selected compound, shown in Table 12, are quite similar during both runs. The only difference between the two runs was the wind speed.

The variability of the predicted emission rates is quite large, with the lower boundary of the 95 percent confidence interval being zero for all compounds.

Comparison of Measured and Predicted Emission Rates

As shown in Table 8, the predicted emission rates of total NMHC exceed all the measured rates for all four surface impoundments tested in this study. The differences are significant in all cases, and very substantial in several. It should be noted that the Thibodeaux, Parker, and Heck emission model was derived for single compounds. A major problem in applying this model to predict total NMHC emissions or emissions of compound groups is the estimation of single physical and chemical parameters to accurately represent the average properties and behavior of multicomponent groups.

The predicted emission rates of compound classes from Reducing Lagoon 1 have been summarized in Table 9 along with the rates measured with the flux chamber. The predicted mean emission rates are generally somewhat higher than those measured with the flux chamber. In some cases, however, the confidence intervals are quite wide and may overlap significantly.

The emission rate as measured with the flux chamber is lower than the predicted rates in the cases where a statistically significant difference is indicated. This trend is in the direction that might be anticipated, since the emission isolation flux chamber does isolate the sampled surface from the wind. The effect of the wind speed is significant in the predictive model. In fact, the model fails at very low or zero wind speed. Thus, it is impossible to strictly compare the emission rate measured with the flux chamber to that predicted by the Thibodeaux, Parker, Heck model, because the predictive model cannot be applied at the conditions inside the flux chamber.

The actual effect of the wind speed on the real emission rate from surface impoundments has not been accurately defined, particularly at the lower wind speeds which existed at the time of testing.

The measured and predicted emission rates of the compound classes from Oxidizing Lagoon 2 are included in Table 10. The predicted values are extremely high compared to the flux chamber results. The primary cause of the high predicted emission rates are the high concentrations of organic compounds found in the liquid samples collected from the Oxidizing Lagoon 2. As previously discussed, oil and oily sludge were present on some parts of the surface of the lagoon. A significant fraction of the organic material was apparently collected with the water samples. Thus, the concentration of organic compounds in the liquid sample, upon which the predicted calculation

is based, was very high. Apparently, the organic layer was not present on the liquid surface which was sampled with the flux chamber.

Table 11 contains a summary of the measured and predicted emission rates of selected compounds and compound classes from Holding Pond 6. There do not appear to be any strong or outstanding trends in the results that would allow definitive conclusions regarding the relative merits of the various methods for estimating emissions. It does appear, however, that the variability of the emission rates is generally less measured with the flux chamber (CV ≃ 30%) than that of the rates measured by the concentration-profile (CV >100%) or the predicted rates (CV >200%).

The summary of the test for statistical differences (Z value) in emission rates is shown in Table 13. It does appear that the concentration-profile (CP) method gives emission rate estimates that are often lower than those measured with the flux chamber or predicted. It also appears that the flux chamber method has some tendency to provide emission rates that are higher than rates determined by the other two methods.

Statistical analyses of the data indicate that the variability of the flux chamber tests appears to be much lower, in general, than those of the concentration-profile and predictive methods. The concentration-profile method tended to give values for Run 1 that were significantly lower, for most compounds, than the rates determined in the latter two test runs. On the other hand, the predicted emission rates for Run 3 were substantially below those predicted for Runs 1 and 2.

The measured and predicted emission rates of selected compounds and compound classes from Spray Evaporation Pond 3 (Site 6) are summarized in Table 12. As mentioned in previous discussions, the transect method should provide an estimate of the total emission rates of the selected compounds, including losses from the spray nozzles and surface evaporation. On the other hand, the emission rates developed with the predictive model apply only to the losses by surface evaporation. Thus, the measured emission rates could be expected to be greater than the predicted rates. Such was not generally the case, however.

For all but one of the selected compounds or compound classes (paraffins), the predicted mean emission rates were higher than the mean measured rates. There are some factors that may be at least partially responsible for these differences:

- The spray nozzles actually force the fine water aerosol particles upward into the air with a considerable velocity. This disturbs the naturally occurring concentration profile above the pond surface. Portions of the plume from the spray nozzles may be carried above the transect sampling points.

- The added vaporization from the spray nozzles may cause significant cooling above the surface of the pond. This

TABLE 13. SUMMARY OF THE TEST FOR DIFFERENCES IN EMISSION RATES FOR HOLDING POND 6, SITE 5

Compound	Run	Statistically Significant Difference Indicated[a]
3-Methylpentane	1	None
	2	None
	3	None
Isobutene + 1-Butene	1	C-P < Predicted
	2	None
	3	C-P < Predicted, Flux Chamber
p-, m-Xylene	1	C-P < Predicted
	2	C-P < Flux Chamber
	3	C-P < Flux Chamber
Toluene	1	None
	[illegible]	Flux Chamber
	3	C-P < Predicted, Flux Chamber
Trichloroethylene + Bromodichloromethane	1	None
	2	C-P < Flux Chamber
	3	C-P < Flux Chamber
Paraffins	1	None
	2	None
	3	None
Total Aromatics	1	None
	2	C-P < Flux Chamber
	3	C-P < Flux Chamber
Total Halogenated HC	1	None
	2	None
	3	C-P < Flux Chamber
Total NMHC	1	None
	2	None
	3	C-P < Flux Chamber

[a]A statistically significant difference in emission rates is indicated from the data at the $\alpha = 0.05$ significance level for z values exceeding 1.96

could cause irregular temperature profiles as well as highly variable temperatures and localized turbulence in the air above the pond.

- Some of the water from the spray nozzles falls back to the surface of the pond. Since this water has been cooled by partial evaporation, the surface of the pond could become subcooled to some extent, inhibiting surface evaporation.

- Some of the spray from the spray nozzles is blown by the wind past the transect sampling points while still in aerosol form. The liquid particles would not be collected in the gas sampling system.

- Finally, it should be restated that the measured emission rates were obtained during borderline meteorological conditions and that the model used to predict the emission rate does not account for spray evaporation, nor the other phenomenon sited above.

While one or more of the above factors could result in some differences between the measured and predicted mean emission rates, the imprecision of the emission rates precludes any definitive conclusions regarding the differences. The wide variabilities in the predicted emission rates are due in part to the variability in the concentrations of the compounds found in pond liquid samples.

LANDTREATMENT SITE

The emission rates of VOC were measured from the landtreatment area at Site 2 with both the concentration-profile method and the emission isolation flux chamber. The emission rates of several selected individual compounds, as well as classes of compounds, were estimated. These measured rates were compared to those predicted with the Thibodeaux-Hwang landtreatment emission model.[19]

The measured and predicted emission rates of selected compounds and groups of compounds are summarized in Table 14.

Measured Rates

Three separate test runs were performed to collect concentration-profile data on the emissions from the landtreatment area. The three runs were made in chronological order, so a decline in the emission rates could be expected in Run 3 as compared to Run 1. This decline occurs because the landtreatment process is not a steady-state process. The concentration of the more volatile compounds in the soil declines with time, since these compounds are continuously lost through volatilization and biological degradation.

TABLE 14. MEASURED AND PREDICTED RATES OF SELECTED COMPOUNDS FROM LANDTREATMENT AREA, SITE 2

Compound or Compound Class	Time from Sludge Application	Measurement Method	Emission Rate, kg-C/hectare-hr		Comments
			Measured	Predicted	
Methylcyclohexane	2.0	FC	1.90 (0.994,3.16)	4.18 (1.74,6.80)	Control Grid Point
	25.0	CP	1.45 (0.846,2.43)	1.19 (0.544,1.90)	--
	26.5	CP	1.26 (0.580,2.10)	1.16 (0.619,1.76)	--
	44.0	CP	0.932 (0.418,2.26)	0.896 (0.479,1.47)	Grid Point 4
	50.0	FC	0.125 (0.0670,0.211)	0.839 (0.339,1.36)	Grid Point 5
	70.0	FC	0.177 (0.0907,0.278)	0.709 (0.355,1.12)	
p-, m-Xylene	2.0	FC	1.27 (0.698,2.00)	6.08 (2.69,10.1)	Control Grid Point
	25.0	CP	2.06 (1.15, 3.64)	1.72 (0.767, 2.71)	--
	26.5	CP	1.68 (0.655, 3.24)	1.67 (0.81,2.83)	--
	44.0	CP	1.38 (0.788, 3.60)	1.30 (0.475,2.15)	Grid Point 4
	50.0	FC	0.0983 (0.0511,0.150)	1.22 (0.598,1.88)	Grid Point 5
	70.0	FC	0.174 (0.0889,0.286)	1.03 (0.446,1.58)	
Toluene	2.0	FC	2.67 (1.37,4.25)	2.20 (1.02,3.27)	Control Grid Point
	25.0	CP	2.54 (1.32,4.28)	0.623 (0.262,1.00)	--
	26.5	CP	1.92 (0.850,3.33)	0.605 (0.240,0.940)	--
	44.0	CP	1.14 (0.551,3.06)	0.468 (0.230,0.785)	Grid Point 4
	50.0	FC	0.103 (0.0472,0.170)	0.439(0.201,0.680)	Grid Point 5
	70.0	FC	0.170 (0.0824,0.264)	0.371 (0.185,0.576)	
Chlorobenzene	2.0	FC	0.504 (0.238,0.749)	4.14 (2.07,6.37)	Control Grid Point
	25.0	CP	0.249 (0.150,0.374)	1.17 (0.637,1.92)	--
	26.5	CP	0.179 (0.0842,0.302)	1.13 (0.464,1.88)	--
	44.0	CP	0.172 (0.0785,0.414)	0.882 (0.436,1.50)	Grid Point 4
	50.0	FC	0.0126 (0.0062,0.0195)	0.828 (0.349,1.33)	Grid Point 5
	70.0	FC	0.0860 (0.0468,0.130)	0.684 (0.326,1.11)	

(Continued)

TABLE 14. (Continued)

Compound or Compound Class	Time from Sludge Application	Measurement Method	Emission Rate, kg-C/hectare-hr		Comments
			Measured	Predicted	
Paraffins	2.0	FC	14.1 (6.70,22.7)	763 (367,1310)	Control Grid Point
	25.0	CP	15.4 (8.96,25.1)	216 (107,330)	--
	26.5	CP	12.6 (5.15,22.8)	210 (94.7,342)	--
	44.0	CP	12.2 (6.77,29.4)	163 (79.2,248)	--
	50.0	FC	1.08 (0.554, 1.63)	153 (74.2,240)	Grid Point 4
	70.0	FC	1.74 (0.842,2.69)	129 (46.1,205)	Grid Point 5
Total Aromatics	2.0	FC	8.78 (4.43,10.2)	551 (255,950)	Control Grid Point
	25.0	CP	20.5 (12.6,32.6)	156 (72.0,259)	--
	26.5	CP	15.7 (6.59,26.5)	152 (71.3,256)	--
	44.0	CP	15.8 (6.55,44.6)	117 (50.4,198)	--
	50.0	FC	0.756 (0.391,1.24)	110 (45.0, 165)	Grid Point 4
	70.0	FC	1.65 (0.806,2.65)	93.2 (35.6,139)	Grid Point 5
Total Halogenated HC	2.0	FC	0.504 (0.230,0.781)	21.4 (10.0,32.4)	Control Grid Point
	25.0	CP	0.249 (0.158,0.425)	6.05 (2.45,10.2)	--
	26.5	CP	0.940 (0.267,2.01)	5.87 (2.71,9.40)	--
	44.0	CP	0.172 (0.0767,0.425)	4.57 (2.31,6.84)	--
	50.0	FC	0.0126 (0.0065,0.0191)	4.28 (2.06,6.98)	Grid Point 4
	70.0	FC	0.0860 (0.0439,0.140)	3.64 (1.81,5.94)	Grid Point 5
Total NMHC	2.0	FC	26.1 (13.6,40.3)	1706 (605,2581)	Control Grid Point
	25.0	CP	45.0 (25.1, 82.4)	482 (206,821)	--
	26.5	CP	34.7 (13.8,61.9)	468 (200,752)	--
	44.0	CP	36.0 (52.6,72.7)	364 (170,583)	--
	50.0	FC	2.19 (1.31,3.21)	341 (126,522)	Grid Point 4
	70.0	FC	4.03 (1.94,6.19)	288 (142,486)	Grid Point 5

As seen in Table 14, the width of the overall 95 percent confidence interval about the measured mean emission rate is generally in the range of ±30-60%, although the uncertainty is somewhat higher for toluene and total halogenated hydrocarbons.

Flux chamber emission measurements were made concurrently with the concentration-profile testing. The resulting measured emission rates are included in Table 14. Because the flux chamber isolates the source from any effects of wind, the measured rates might be expected to be lower (if there is any difference at all) than the emission rates from the sources exposed to the weather.

The emission rates of compounds from landtreatment areas are time-dependent. The maximum emission rate can be expected close to the time of initial sludge application. From that time forward, the emission rate should decline with time, provided no additional sludge is applied and the landtreatment area is generally undisturbed. At Site 2, the landtreatment area was raked/tilled on a daily basis. The emission rates can be expected to rise during the tilling and for a short period after tilling. The overall downward trend in emission rates should still exist, however. This trend is generally observed in the rates summarized in Table 14. The flux chamber measurement at the Control Point was made about 2 hours after sludge application. At that time, the measured emission rates of all the compounds were very much above those measured at later times.

The rates measured at Grid Point 5 were consistently higher than those determined at Grid Point 4. This is evident in spite of the fact that the flux chamber measurements were made at Grid Point 5 some 20 hours after those made at Grid Point 4. The method of spreading the sludge at Site 2 generally appeared to result in a somewhat uneven application throughout the landtreatment area. The uneven application may be responsible for the higher emission rates measured at Grid Point 5.

Because of the time-dependent nature of the emission rates from the landtreatment area, the rates measured by the flux chamber technique should not be compared precisely to those estimated by the concentration-profile method.

Predicted Emission Rates

Samples of the sludge-laden soil were collected and analyzed to determine the concentration of organic species in the soil. Emission rates were then calculated at six selected times using the Thibodeaux-Hwang model. The selected times corresponded to the times at which emission rates from the landtreatment area were measured by either the flux chamber or concentration-profile techniques. The predicted rates are included in Table 14. The predicted rates for the various compounds or compound classes vary over several orders of magnitude. The highest predicted emission rates occur for paraffins and total aromatics. These groups of compounds are present in the highest concentrations in the soil.

Comparison of Measured and Predicted Emission Rates

The emission rates measured with the flux chamber at the elapsed time of 70 hours are consistently higher than those measured at 50 hours by the same measurement methods. The majority of flux chamber measurements were made over a period when the emission rate from the landfarm was expected to be constant (50-70 hours elapsed time). The probable explanation for this particular phenomenon is that the rates were measured at two different points on the surface of the landtreatment area. As discussed earlier, the sludge was not spread in a particularly homogeneous fashion. Thus, it is very possible that a higher concentration of sludge was present at Grid Point 5 than at Grid Point 4.

As shown in Table 14, the predicted emissions compared favorably with the measured emission rates (particularly for concentration-profile measurements) for specific compounds; however, agreement was poor for the compound classes. In all cases for the compound classes, the predicted emission rates were much greater than the measured rates. This difference can probably be attributed to a problem of determining composite parameters for the compound classes. In general, the flux chamber measurements resulted in emission rates which were lower than the predicted rates and the rates measured by the CP. Although the CP-measured rates were higher than those measured with the flux chamber, they were still significantly below the predicted rates for the compound classes. The agreement between the predicted rates and those determined by the CP was much better for the individual compounds.

A possible contributing factor to the higher rates measured by the concentration-profile method is the tilling of the landtreatment site. The site was tilled at about 19 hours after sludge application. Immediately after tilling, the emission rates can be expected to increase. The increase in emission rates immediately after tilling is due to the mixing of the soil-sludge during tilling. Material containing oil and volatile species is brought to the surface. Volatile compounds are lost at a more rapid rate from the soil near the surface. Since two of the concentration-profile measurements were taken 6-7 hours after tilling, some increase in emission rates over that predicted by the model (assuming no effect of tilling) is not surprising.

The somewhat scattered data and the wide confidence intervals preclude any really definitive conclusions regarding the relative accuracies of the one predictive method and the two measurement methods.

LANDFILLS AND LANDFILL VENTS

The emissions from the surface of active landfills were measured with the flux chamber and transect techniques. The five sampled active landfills include:

- Site 2: Active Landfill
- Site 4: Active Chemical Landfill D

- Site 5: Active Landfill 10: Flammable Cell
  Active Landfill 10: Toxic Cell
  Active Landfill 10: General Organic Cell

The measured emission rates of selected compounds and compound classes are summarized in Tables 15 and 16. Existing predictive landfill models require that the vapor composition in the vicinity of the buried wastes be known. The landfills examined in this study included a mix of drummed and bulk waste of varying compositions. Additionally, the depths of the waste layers were variable and quite substantial. For these reasons, it was not possible to develop an accurate estimate of the overall waste composition. It should be noted that current landfill models do not account for vents.

Site 2: Active Landfill

Emission rates were determined by both the transect method and flux chamber measurements at the Site 2 active landfill. The transect data for the detected compounds were very widely scattered. Most of the detected compounds were not considered for emission rate estimation because of low concentrations or because concentrations were absent at one or more of the transect test points. The transect concentration data for those few compounds or compound classes shown in Table 15 were still very scattered. The concentration profiles were quite irregular, and normal curves could be fitted to these data only with some difficulty and considerable uncertainty.

As shown in Table 15, the transect measured emission rates estimated with Method 1 procedures are generally higher than those determined by the Method 2 technique. The relative accuracies of the emission rates estimated by the two different methods are not known. The emission rates of acrylonitrile are not consistent for the three transect runs. This is the only compound for which multi-run transect data are available.

The confidence intervals are quite broad, reflecting at least in part, the relative inaccuracy of the fitted normal curves in simulating the actual concentration profiles.

Flux chamber measurements were performed at two grid points. The emission rates of the compounds generally agree quite well between the two sampling points. The rates are quite low for most of the individual compounds.

The rates measured with the flux chamber appear to be very much lower than the rates of those three compounds (acrylonitrile, paraffins, total halogenated HC) estimated by the transect method. The difference is very substantial, several orders of magnitude. No explanation is readily evident for this difference. The transect testing in general, however, gave very poor and erratic results for this particular source. The precision of the flux chamber measurements was considerably better than that associated with the transect measured emission rates.

TABLE 15. MEASURED EMISSION RATES OF SELECTED ORGANIC COMPOUNDS FROM ACTIVE LANDFILL: SITES 2 AND 4

Compound or Compound Class	Run No.	Site 2: Active Landfill — Transect Measurements — Emission Rate, kg-C/hectare-hr		Site 2: Active Landfill — Flux Chamber Measurements		Site 4: Active Chemical Landfill D	
		Method 1	Method 2	Grid Point	Emission Rate, kg-C/hectare-hr	Grid Point	Emission Rate, kg-C/hectare-hr (95% Confidence Interval)
Methylcyclohexane	--	--	--	2	0.00003 (0.0000,0.00005)	--	--
				10	0.00013 (0.00006,0.00021)		
Toluene	--	--	--	2	0.00013 (0.00006,0.00620)	--	--
				10	0.00006 (0.00003,0.00010)		
p-, m-Xylene	--	--	--	2	0.00010 (0.00005,0.00017)	--	--
				10	0.00007 (0.00003,0.00019)		
Chlorobenzene	--	--	--	2	0.00011 (0.00006,0.00017)	--	--
				10	0.00004 (0.00002,0.00007)		
Acrylonitrile	1	0.133 (0.081,0.565)	0.134 (0.044,0.619)	--	--	--	--
	2	0.0774 (0.0444,0.233)	0.0543 (0.0180,0.114)				
	3	0.0113 (0.050,1.56)	0.0890 (0.0230,0.207)				
Paraffins	3	1.00 (0.154,124.8)	0.211 (0.065,0.608)	2	0.0082 (0.0035,0.0343)	1	0.0407 (0.0172,0.0684)
				10	0.0221 (0.0098,0.0343)		
Olefins	--	--	--	2	0.0112 (0.0060,0.0169)	1	0.0275 (0.0111,0.0425)
				10	0.0109 (0.0060,0.0169)		
Total Aromatics	--	--	--	2	0.0066 (0.0036,0.0104)	1	0.0706 (0.0303,0.120)
				10	0.0041 (0.0022,0.0066)		
Total Halogenated HC	3	0.0532 (0.032,0.410)	0.0390 (0.0102,0.112)	2	0.00011 (0.00006,0.00018)	1	0.0302 (0.0133,0.0522)
Total NMHC	--	--	--	2	0.0277 (0.0157,0.0424)	1	0.169 (0.0814,0.301)
				10	0.0395 (0.0209,0.0601)		

TABLE 16. MEASURED EMISSION RATES OF SELECTED ORGANICS FROM ACTIVE LANDFILLS - SITE 5

Compound or Compound Class	Landfill 10: Flammable Cell				Landfill 10: Near Toxic Cell				Landfill 10: Organic Cell	
	Transect Measurements			Flux Chamber Measurements	Transect Measurement			Flux Chamber Measurements		
	Run No.	Emission Rate, kg-C/hectare-hr Method 1	Method 2	Grid Point	Emission Rate, kg-C/hectare-hr	Run No.	Emission Rate, kg-C/hectare-hr Method 1	Method 2	Grid Point	Emission Rate, kg-C/hectare-hr
Methylcyclohexane	1	0.0027(0.00066,0.0120)	0.0037(0.0022,0.0183)	--	--	--	--	--	--	--
2,4-Dimethylpentane				--	--	3	0.0142(0.0025,0.0468)	0.0216(0.0180,0.0346)	--	--
Toluene	1	0.0709(0.0159,0.217)	0.0990(0.0432,0.544)	--	--	2	0.0253(0.0094,0.0544)	0.0323(0.0230,0.0515)	--	--
						3	0.0655(0.0167,0.115)	0.090(0.0626,0.120)		
p-,m-Xylene	1	0.0144(0.0033,0.0432)	0.0237(0.0119,0.130)	--	--	2	0.0188(0.0047,0.0374)	0.0245(0.0177,0.0389)	--	--
						3	0.0343(0.0121,0.0662)	0.0461(0.0320,0.0641)		
1,1,1-Trichloroethane	1	0.0011(0.0004,0.0036)	0.0014(0.0010,0.0027)	--	--	3	0.0213(0.0060,0.0472)	0.0320(0.0217,0.0598)	--	--
Paraffins	1	0.0308(0.0087,0.0922)	0.0418(0.0247,0.185)	4	0.0259 (0.0126,0.0407)	3	0.0569(0.0112,0.103)	0.0785(0.0529,0.115)	6	0.198(0.0673,0.0340)
									7	0.0303(0.0135,0.0518)
Olefins				4	0.102 (0.0045,0.0169)	3	0.0203(0.0059,0.0529)	0.0284(0.0188,0.0526)	6	0.0641(0.0332,0.102)
									7	0.0049(0.0018,0.0083)
Total Aromatics	--	--	--	4	0.117 (0.0378,0.189)	2	0.140(0.0385,0.446)	0.184(0.123,0.522)	6	0.244(0.104,0.392)
						3	0.192(0.0547,0.378)	0.261(0.177,0.353)	7	4.48(1.81,7.56)
Total Halogenated HC	1	0.0078(0.0016,0.0204)	0.0103(0.0072,0.0261)	4	0.0385 (0.0185,0.0634)	2	0.0544(0.0103,0.180)	0.0727(0.0421,0.356)	6	0.0219(0.0096,0.0371)
						3	0.112(0.0301,0.229)	0.163(0.102,0.267)	7	0.0008(0.0004,0.0017)
Total NMHC	1	0.157(0.0468,0.468)	0.224(0.114,1.16)	4	0.195 (0.0896,0.315)	3	0.385(0.0792,0.683)	0.529(0.360,0.806)	6	0.554(0.245,0.871)
									7	4.54(1.84,7.60)

Site 4: Active Chemical Landfill D

Flux chamber measurements were made at only one location on the surface of Active Chemical Landfill D at Site 4. The results of this single test are shown in Table 15. The precision of the individual measurements appears to be reasonable and comparable to other flux chamber results at comparable concentration levels.

Site 5: Active Chemical Landfill 10, Flammable Cell

Emission rates were determined by both the transect method and flux chamber measurements at the flammable cell of Landfill 10. The results are presented in Table 16.

The transect concentration data varied considerably in approaching normal distributions. In some cases, a normal curve could not practically be fitted to the concentration profile. It was impossible to estimate emission rates in these cases.

The emission rates were estimated from the transect data by the two methods described previously in this section of the report. The emission rates calculated by Method 2 are consistently higher, by a factor of 1-2.5, than those estimated by Method 1. It is not possible at this time to define which of the two estimating methods provides the most accurate emission rate. The confidence intervals generally appear to be somewhat broader for the Method 2 results. The width of these intervals reflects, in part, the accuracy of the fitted curve in describing the actual profile.

Emission measurements were performed at one point in the flammable cell. The results are shown in Table 16. The agreement between the transect results and the flux chamber results appears quite good for the only three common compound groups (paraffins, total halogenated HC, and total NMHC). The precision of the flux chamber measurements is considerably better, however.

Site 5: Active Chemical Landfill 10, Toxic Cell

Transect Runs 2 and 3 were performed near the toxic cell of Landfill 10. This cell was at the opposite end of the landfill area from the flammable cell. Results are shown in Table 16. With a few exceptions, the emission rates for those compounds common to Runs 1, 2, and 3 are similar in magnitude. The same consistently higher rates are seen here also with the Method 2 estimations. In general, it appears that the precision of the estimated emission rates is somewhat better than observed in other transect runs.

Site 5: Active Chemical Landfill 10, General Organic Cell

Only flux chamber measurements were performed at the General Organic Cell. The results are included in Table 16. Only the emission rates of the major hydrocarbon classes of compounds were determined. The emission rates

of compound classes vary widely between the two sampling points (6 and 7). The precision of the emission rates is reasonably good, however. The emission rates of all compound classes except total aromatics are considerably higher at point 6, but the emission rate of total aromatics from point 7 is very much higher than any of the other rates or even the sum of all the other rates at point 6.

STORAGE TANKS

Emissions from storage tanks were only investigated at Site 6. Storage tanks at Site 6 were vented directly to the atmosphere through ∿2-inch diameter lines. Although screening at the vent outlets indicates the presence of hydrocarbons, the apparent flow rates through the vents were too low to measure with available instruments (hot wire anemometer, bubble meter). Storage tank emission models were used to estimate breathing losses from four of the tanks at Site 6. The results are shown in Table 17.

DRUM STORAGE

The drum storage building at Site 5 was enclosed and vented. The exhaust air from this building was sampled to provide a measure of the emission rates from the stored drums. The measured emissions of total NMHC was 105 kg/year, with halogenated hydrocarbons accounting for 65 percent of the emissions.

At other sampling sites, drums were stored outside. It was not possible to get an estimate of emissions because of the location of the drum storage areas and prevailing meteorological conditions at the time of sampling.

SOLVENT RECOVERY PROCESS

During the testing at Site 6, two solvents were purified by distillation. These were methyl ethyl ketone (MEK) and 1,1,1-Trichloroethane (TCE). Direct measurement of emissions was not practical, so volumetric measurements of feedstocks and products were made during each purification. These measurements, combined with liquid density and chemical analysis results, allowed overall material balances to be made for each run.

The purification of MEK was a simple single-step distillation process performed under vacuum in a Luwa thin-film evaporator. Hydrocarbon losses occurred at the column vacuum pump vent and during transfer of the bottoms into drums. A material balance indicated a small loss of about 64 (-712, 952) kg during the distillation. This loss represents about 1.1% (-12.8%, 14.6%) of the feedstock. The uncertainties are large, however, due to the imprecision of volumetric measurements (primarily liquid levels).

Spent TCE was purified in a two-step process. The TCE was first distilled under vacuum in the Luwa evaporator. The distilled product was then washed with water to remove any water-soluble compounds which may have been distilled along with the TCE. The washing was accomplished in an agitated

TABLE 17. PREDICTED EMISSION RATES OF VOLATILE ORGANIC COMPOUNDS FROM FOUR FIXED-ROOF TANKS, SITE 6

Tank ID	Volatile Organic Compounds Stored in Tank	Predicted VOC Emission Rate, kg/year
T-14	Acetone, methyl ethyl ketone, methanol	23
T-15	Methylene chloride, freon, trichloroethylene 1,1,1-trichloroethane, toluene	88
T-16	n-Methylpyrrilidone	44
T-17	Methanol, acetone, methyl ethyl ketone, toluene	18

vessel. After agitation, the water and organic phases were given time to separate. The lighter water phase was removed by manually maneuvering a flexible pump suction hose through an open manway in the mixing vessel and into the water phase.

A material balance indicated TCE losses of 202 (-1437, 1624) kg during the distillation and 2797 (880, 4204) kg during the washing. The total losses are equivalent to about 17.9% (-3.3, 34.8) of the feedstock. Although the confidence intervals are very wide, it does appear that the losses during the washing step are considerably greater than the losses during distillation. It seems probable, from an analysis of the process, that a significant volume of TCE was removed with the wash water during the manual skimming of the water phase from the TCE phase. TCE removed with the wash water will be transferred to the spray evaporation pond. There, the TCE must either be vaporized or degraded by oxidation.

SECTION 7

DATA QUALITY

There is always some amount of uncertainty associated with any measurement data due to inherent limitations of the system used to make the measurements. The usefulness of the measurement data is dependent to some extent upon the degree to which the magnitude of this uncertainty is known and upon its relative impact. The HWDF testing described in this report included a comprehensive quality assurance/quality control (QA/QC) program. The objectives of the QA/QC efforts were twofold. First, they provided the mechanism for controlling data quality within acceptable limits. Second, they form the basis for estimates of uncertainty by providing the necessary information for defining error limits associated with the measurement data.

The quality control part of the QA/QC effort consisted of numerous procedures designed to provide ongoing checks of the primary components of the various measurement systems. Examples of these procedures include instrument calibration checks, linearity checks (i.e., multipoint calibrations), instrument drift checks, control standard analyses, duplicate analyses, etc. These procedures are described in detail in the Test Plan/Quality Assurance Project Plans prepared for each site[21,22,23], along with required frequencies and acceptance criteria for each QC check.

The evaluative part of the QA/QC effort was designed to fulfill two related objectives. First, it provided an assessment of the adequacy of the internal QC system used in the day-to-day sampling/analytical efforts. Second, it was designed to provide a basis for quantitative estimates of uncertainty in the measurement data. An on-site QA audit, conducted by the project QA Coordinator during testing at Site 5, played an important role in achieving both of these objectives. The qualitative systems audit consisted of a detailed evaluation of the overall effectiveness of the internal QC system. The accompanying performance audit represented a quantitative, point-in-time assessment of the capability of the various measurement systems to generate data of acceptable quality. Performance audit results, along with results for duplicate samples, also represented a basis for quantitative estimates of uncertainty in the measurement data. Uncertainty estimates for individual measurements, such as ambient concentration of a particular class of VOC compounds, for example, provided the basis for estimates of overall uncertainty in measured and/or predicted emission rates. These uncertainty estimates enabled the calculation of confidence intervals for the reported emission rates and variability estimates for the measurement approaches and models.

Detailed results of the QA audit were presented in the Data Volume for Sites 4 and 5[1]. Confidence interval estimates for reported emission rates are presented elsewhere in this document and in the individual data volumes[1,2,3]. This section presents a summary of the performance audit results, along with a summary of variability estimates used to derive the confidence interval estimates. Audit results and precision estimates for the various measurement parameters are summarized in Table 18, and discussed in more detail below.

MEASUREMENT VARIABILITY

With any measurement effort, a primary data quality consideration is measurement variability, or precision. For this program, duplicate samples and/or analyses were used to quantitate sampling and analytical variability for the various measurement parameters. The resulting precision estimates represent the amount of variability which was due to random error in the sampling/analytical process, independent of actual variability in the parameter measured.

Flux Chamber Measurements

Flux chambers were used to make direct emission measurements. Two sampling/analytical techniques were used in this measurement approach. One technique consisted of collecting samples in evacuated stainless steel canisters which were then returned to Austin for GC analysis. The other technique involved collecting samples in a gas syringe for on-site analysis by GC-FID. Duplicate flux chamber samples were collected using the syringe sampling technique at Site 2 and Site 5. Twelve syringe samples collected during the program were analyzed in duplicate (i.e., duplicate analyses of a single sample). Results for duplicate analyses were used to estimate analytical precision for the on-site GC analyses. Results for duplicate samples were used to estimate overall sampling and analytical variability of the VOC concentration measurements associated with the flux chamber technique. Precision estimates are summarized in Table 19.

The precision estimates shown in Table 19 are expressed in terms of pooled (i.e., "average") coefficients of variation for duplicate samples and duplicate analyses. The coefficient of variation represents the standard deviation of the measured values expressed as a percentage of the mean. Two estimates are presented for each class of compounds. One is for species in each class (e.g., paraffin species), and represents the pooled CV for individual compounds in that class. The other estimate represents the precision, or variability, for class totals (e.g., total paraffins).

Separate estimates of precision for flux chamber canister samples are not available since no duplicate canister samples were collected.

Indirect Measurement Methods

The two primary methods for indirect emission rate measurements were the concentration-profile (C-P) and transect techniques. Both of these

TABLE 18. SUMMARY OF MEASUREMENT DATA QUALITY

Measurement Parameter	Performance Audit Results				Precision Estimates			
	Mean Error[a] (Bias)	Audit Range[b]	Range of Relative Error[c]	Accuracy Objectives[d]	Sampling Plus Analytical Variability[e] (%)	Analytical Variability[f] (%)	Mean Measured Concentration	Precision Objectives[g]
Screening Measurements								
HNU	0.08 ±0.02 ppmv	0.0-1.99 ppmv	+5% to +60%	±100%	h	h		
OVA	44 ±30 ppmv	12-28 ppmv	+100% to +206%	±100%	h	h		
Shimadzu	0.0 ±0.9 ppmv	0.0-112 ppmv	-40 to +33%	±100%	h	h		
Flux Chamber Measurements								
VOC Concentration								
Gas Syringe Samples	-1.4 g/m^2-sec[i]	26.5 g/m^2-sec	5.3%[i]	±100%	61.2[j]	18.6[j]	1626 ppmv-C	50%
Canister Samples	-1.7 g/m^2-sec[i]	26.5 g/m^2-sec	6.4%[i]	±50%				
Indirect Measurements								
VOC Concentration								
Concentration-Profile	2.5 ±6.6 ppmv-C	4.4-368 ppmv-C	-45.9% to 53.5%	±50%	32.5	8.2	15904 ppbv-C	30%
Transect	2.5 ±6.6 ppmv-C	4.4-368 ppmv-C	-45.9% to 53.5%	±50%	123[h]	19.6[h]	1238 ppbv-C	30%
Temperature	-0.1 ±0.1°F	0-120°F	-1.7% to 0%	±5%				
Windspeed	-0.2 ±0.2 mph	10-100 mph	-4% to +4%	±10%	h	h		
Predictive Techniques								
VOC Concentration								
Liquid Samples	5.3 ±8.5 g/l	6.5-60 g/l	-81.6% to +222%	±100%	45.5	1.1	4223 ng-C/ml	30%
Solid Samples	1.0 ±0.7% recovery	4-20 g/g	-99.9% to -97.9%	±200%	54.5[h]	54.5[h]	12802 ng-C/ml	50%
Moisture Content	-0.2% to 0.0%	7.2-15.2 wt%	-1.3% to 0%	±20%				

[a] 95% confidence interval for mean error.
[b] Range over which the indicated measurement system is audited.
[c] Range of observed relative error (i.e., accuracy) for the performance audits.
[d] Objectives presented in the Quality Assurance Project Plan, where accuracy represents total relative error for a single measurement, including both systematic error (bias) and random error (variability due to imprecision).
[e] Coefficient of variation (i.e., relative standard deviation) for duplicate samples; represents total variability of the measurement process.
[f] Coefficient of variation for replicate analyses of individual samples; represents analytical variability independent of sampling variability.
[g] Objectives presented in the Quality Assurance Project Plan, where precision represents coefficient of variation for replicate determinations.
[h] Not required for calculation of confidence intervals for emission rate.
[i] Based on a single sample.
[j] No duplicates available; estimated precision of 35%.

TABLE 19. PRECISION ESTIMATES FOR FLUX CHAMBER/GAS SYRINGE SAMPLE RESULTS

Hydrocarbon Class[a]	Mean Conc. (ppmv-C)	Sampling Plus Analytical[b] (%)	Analytical[c] (%)
Paraffin Species	51.2	30.7 (25.5)	26.5 (20.3)
Total Paraffins	192.1	113.2	23.8
Olefin Species	15.8	28.6	15.9
Total Olefins	20.9	28.6	47.9
Aromatic Species	119.5 (128.5)	34.0	36.2 (21.9)
Total Aromatics	194.0	34.9	32.1
Halogenated HC Species	138.0	--	11.0
Total Halogenated HC	138.0	--	11.0
All Species[d]	66.0 (67.1)	31.7 (28.0)	22.7 (19.9)
Total NMHC[d]	1626.1	62.1	18.6

[a]Species CV represents agreement between replicate values for summation of identified species of the class indicated; CV for total reflects agreement of values for class totals based on total peak area for a given class.

[b]Estimate of total variability in sampling/analytical process, based on results for duplicate samples.

[c]Estimate of analytical variability, independent of sampling variability, based on results for duplicate analyses.

[d]Excludes oxygenated HC species.

techniques involved collection of air samples in evacuated canisters, with off-site GC/FID-PID/HECD analysis. For both measurement methods, duplicate canisters were collected at one sampling location for each run. Six C-P canisters were also analyzed in duplicate, as were eight of the transect canister samples. Precision estimates based on these duplicate samples and duplicate analyses are summarized in Tables 20 and 21 for the C-P and transect samples, respectively.

As indicated in the tables, overall (i.e., sampling plus analytical) precision was much better for the C-P technique than for the transect technique. Although analytical CVs were consistently lower for the C-P technique (i.e., measured precision was better), the differences between the two techniques were small for analytical variability alone. This indicates that sampling variability played a significant part in the greater overall variability for the C-P technique.

Predictive Techniques

A common feature of most of the predictive models used in this program (except for API storage tank losses models) was a term for concentration of one or more VOC species in either a solid (e.g., landfill,landfarm) or liquid (e.g., surface impoundment) phase. The Thibodeaux, Parker, and Heck model for surface impoundments, for example, includes a term X_i, which is the mole fraction of component i in the aqueous phase. Values used for these concentration terms were based on analytical results for solid or liquid samples, as appropriate. Estimates of variability, or precision, for these values are based on results for duplicate samples and duplicate analyses.

Of the duplicate liquid samples collected, both samples of two duplicate pairs were analyzed. One pair was collected at Site 5 (Lagoon #1) and one pair at Site 6 (Evaporation Pond). Results for these samples were used to derive the precision estimates shown in Table 22. Precision estimates for solid samples, shown in Table 23, are based on results for a single pair of duplicate solid samples collected at the Site 2 landfarm, and two pairs of duplicate analyses.

MEASUREMENT ACCURACY

As part of the quality assurance effort for this program, performance audits were conducted concurrently with sampling and analytical efforts for Site 5. These audits, performed by the QA Coordinator, were intended to provide a direct, point-in-time evaluation of the capability of the measurement system to generate data of acceptable quality. In its broadest sense, the measurement system consisted of numerous components, including the equipment, apparatus, calibration standards, and personnel used to perform the testing, as well as the associated procedures and techniques used for sample collection, sample analysis, and data reduction. The performance audits, which included both on- and off-site activities, generally consisted of challenging selected measurement system components with audit standards

TABLE 20. PRECISION ESTIMATES FOR C-P CANISTER SAMPLE RESULTS

Hydrocarbon Class[a]	Mean Conc. (ppmv-C)	Sampling Plus Analytical[b] (%)	Analytical[c] (%)
Paraffin Species	224.0	24.6	11.8 (10.4)
Total Paraffins	6060.5	30.7	9.2
Olefin Species	94.5	26.1	20.6 (18.9)
Total Olefins	2896.3	32.9	31.4 (13.5)
Aromatic Species	319.9	33.8	15.5 (14.4)
Total Aromatics	6821.9	34.5	10.4
Halogenated HC Species	52.7	27.2	13.8 (8.6)
Total Halogenated HC	106.0	27.2	7.3
All Species[d]	212.6	27.9	15.6 (14.5)
Total NMHC[d]	15904.0	32.5	8.2

[a]Species CV represents agreement between replicate values for summation of identified species of the class indicated; CV for total reflects agreement of values for class totals based on total peak area for a given class.

[b]Estimate of total variability in sampling/analytical process, based on results for duplicate samples.

[c]Estimate of analytical variability, independent of sampling variability, based on results for duplicate analyses.

[d]Excludes oxygenated HC species.

TABLE 21. PRECISION ESTIMATES FOR TRANSECT TECHNIQUE GAS CANISTER SAMPLE RESULTS

Hydrocarbon Class[a]	Mean Conc. (ppmv-C)	Sampling Plus Analytical[b] (%)	Analytical[c] (%)
Paraffin Species	34.2	118.0	23.7 (15.5)
Total Paraffins	487.9	153.9	10.2
Olefin Species	8.8	72.2	30.5 (26.9)
Total Olefins	107.9	103.4	19.9
Aromatic Species	35.8	77.4 (70.7)	20.5 (12.3)
Total Aromatics	416.4	130.7	42.9
Halogenated HC Species	105.4	121.0	16.6 (13.2)
Total Halogenated HC	423.4	79.8	12.2
All Species[d]	36.9	98.5 (96.6)	24.7 (18.5)
Total NMHC[d]	1238.4	123.0	19.6

[a]Species CV represents agreement between replicate values for summation of identified species of the class indicated; CV for total reflects agreement of values for class totals based on total peak area for a given class.

[b]Estimate of total variability in sampling/analytical process, based on results for duplicate samples.

[c]Estimate of analytical variability, independent of sampling variability, based on results for duplicate analyses.

[d]Excludes oxygenated HC species.

TABLE 22. PRECISION ESTIMATES FOR LIQUID SAMPLE RESULTS

Hydrocarbon Class[a]	Mean Conc. (ppmv-C)	Sampling Plus Analytical[b] (%)	Analytical[c] (%)
Paraffin Species	15.5	61.7	28.3
Total Paraffins	160.5	40.4	13.2
Olefin Species	13.1	51.3 (27.3)	11.7
Total Olefins	203.4	41.6	24.8
Aromatic Species	100.2	39.9	26.1 (10.4)
Total Aromatics	1174.6	16.4	2.8
Halogenated HC Species	241.4	61.0	16.0
Total Halogenated HC	2530.0	56.7	2.3
All Species[d]	100.7	53.9	22.9 (16.8)
Total NMHC[d]	4222.8	45.5	1.1

[a]Species CV represents agreement between replicate values for summation of identified species of the class indicated; CV for total reflects agreement of values for class totals based on total peak area for a given class.

[b]Estimate of total variability in sampling/analytical process, based on results for duplicate samples.

[c]Estimate of analytical variability, independent of sampling variability, based on results for duplicate analyses.

[d]Excludes oxygenated HC species.

TABLE 23. PRECISION ESTIMATES FOR SOLID SAMPLE RESULTS

Hydrocarbon Class[a]	Mean Conc. (ppmv-C)	Sampling Plus Analytical[b] (%)	Analytical[c] (%)
Paraffin Species	427.0	36.7	42.7
Total Paraffins	4518.7	20.3	91.5
Olefin Species	446.8	31.4	58.9 (45.8)
Total Olefins	3167.2	16.0	43.9
Aromatic Species	289.1	62.3 (38.6)	54.4 (51.2)
Total Aromatics	4399.9	29.1	41.2
Halogenated HC Species	164.6	--	36.6
Total Halogenated HC	687.2	--	28.9
All Species[d]	351.8	50.4 (36.4)	51.9 (47.3)
Total NMHC[d]	12801.6	16.0	54.5

[a]Species CV represents agreement between replicate values for summation of identified species of the class indicated; CV for total reflects agreement of values for class totals based on total peak area for a given class.

[b]Estimate of total variability in sampling/analytical process, based on results for duplicate samples.

[c]Estimate of analytical variability, independent of sampling variability, based on results for duplicate analyses.

[d]Excludes oxygenated HC species.

and comparing measured values to reference values. Audit procedures and results are discussed below.

Meteorological Measurements

Wind speed and air temperature sensors were used to provide the meteorological data necessary for application of both the concentration-profile and transect techniques of indirect emission measurement. Performance audits of the meteorological systems were performed at Radian's Austin laboratory, just prior to deployment of the equipment to the field. For the wind speed audit, using a calibrated frequency generator, all of the six sensors responded within $\pm$2 mph over the audit range of 10 to 100 mph. Four of the six sensors responded within $\pm$1 mph at all audit points, and mean error for all sensors was within $\pm$1 mph. Performance audits of the six temperature sensors were performed using an NBS-traceable decade resistance unit to input known resistances to the temperature sensor translators. All temperature sensor translators responded within $\pm$1°F over the audit range (0° to 120°F). Four of the six were 1°F low at 60°F.

On-Site Measurements

Three portable analyzers were used for on-site analyses. An OVA and an HNU analyzer were generally used as screening instruments to define relative differences in concentration over time or from point to point. A Shimadzu GC was used for rudimentary speciation and quantitation of gas-syringe grab samples.

On-site performance audits were conducted on all three analyzers during testing at Site 5. These audits consisted of challenging the analyzers with various concentrations of audit gas mixtures.

The HNU audit was performed by diluting an EPA benzene standard to five concentrations ranging from 0.20 to 1.99 ppmv. A zero point was also run, using hydrocarbon-free air. Analyzer linearity was very good (correlation coefficient >0.999) and the largest measurement error observed was 0.12 ppmv.

The OVA audit was performed using dilutions of another EPA audit standard. The multipoint audit covered the concentration range from 12 to 28 ppmv benzene. Since the OVA was calibrated using methane, the measured concentrations are meaningful only as indicators of relative response to different concentrations. The correlation coefficient of 0.9961 indicates that, over the audit range, the OVA response was acceptably linear for the screening function which the instrument performed.

The performance audit of the Shimadzu GC consisted of two parts. First, a multipoint audit using benzene was performed over the range of 1.0 to 112 ppmv (plus zero). The largest observed error was 3.0 ppmv (low) at an input concentration of 112 ppmv. Overall, mean error was 0.0 $\pm$0.9 ppmv, and the correlation coefficient was >0.999.

The second part of the Shimadzu audit consisted of challenging the analyzer with a mixture containing C_2 to C_{10} normal alkanes plus iso-pentane, benzene, and toluene. All species except decane were detected and correctly identified. Decane was not detected because it did not elute within the normal analysis time. Quantitatively, the results were adequate for the intended purpose of this instrument, that being to provide rapid, on-site, semi-quantitaive data for individual sample components. Error ranged from 53% high for ethane to 35% low for nonane, with a mean relative error of 0.2 $\pm$15.3%.

Off-Site GC Analyses

A Varian 3700 GC system was used for off-site analysis of canister samples, liquid samples, and soil/waste samples. Performance audits of this system addressed each of the three sample types.

The performance audit for the canister sample analyses consisted of submitting for analysis two canisters containing audit gas mixtures. Both canisters were filled during the field audit, and shipped and handled in the same manner as the field samples. One of the two audit canisters was loaded with a standard containing 0.254 ppmv benzene. This sample was analyzed in duplicate and a value of 0.247 ppmv benzene was reported for both analyses based on FID/PID quantitation, for an error of -0.007 ppbv or -2.8%.

The second audit canister was loaded with the same multicomponent hydrocarbon standard as used for the Shimadzu audit. Overall, results for two analyses of this sample were quite acceptable, with detection of all components, 100% correct identification, and all error values with the acceptability limits for canister sample analyses.

The performance audit of liquid sample analyses consisted of submitting two EPA Water Pollution Quality Control Samples (WP 1079 Halogenated Purgeables) for analysis. Each sample contained eight compounds, and the two samples were at different concentrations. Results for these analyses were within the 95% confidence interval for measured recovery reported by EPA for all compounds except t-1,2-dichloroethylene in Sample 2 and chloromethane and chloroethane in both samples. Extremely high (>100%) results for chloromethane and chloroethane indicated a problem in the calibration standard being used for the HECD.

In addition to canister samples and liquid samples, the Varian GC system was also used for analysis of solid samples of soil and/or waste. The audit of these analyses consisted of submitting a sample of silica (sand) spiked with a solution containing eight purgeable organics. All but one compound was detected and correctly identified. Bromodichloromethane was apparently misidentified as trichloroethylene. Although rather good qualitative results were obtained, recoveries were extremely low, ranging from 0.1% to 2.1%. Based on these data, it would be reasonable to conclude that concentrations reported for organic species observed in the soil/waste samples probably represent very conservative estimates of the "true" concentration in the original, undisturbed sample. Actual concentrations were

possibly two to three orders of magnitude higher than that reported. However, since the relationship between concentration in the soil/waste sample and potential for emission into the air is not straightforward and would be expected to vary depending upon physical characteristics of the substrate, these data must be interpreted with caution.

Flux Chamber Measurements

Isolation flux chambers were used in conjunction with the portable analyzers as well as the canister sampling/GC analysis technique to make direct emission measurements. Audit results presented above for the on-site analyses and off-site canister sample analyses provide estimates of analytical uncertainty for these data. They do not, however, address the potential effect of the flux chamber itself upon sample collection. In order to address this potential, one of the EPA benzene audit standards was introduced into the flux chamber at a constant, known flow rate. Two samples of the chamber effluent were then collected, one by the canister technique and one using the gas syringe grab sampling technique. The syringe sample was analyzed on site using the Shimadzu GC, while the canister sample was returned to Austin and analyzed using the Varian GC system.

The true concentration of benzene in the flux chamber was 23.3 ppmv. The initial Shimadzu analysis of the syringe sample indicated a concentration of 22.2 ppmv, or 1.1 ppmv low (-4.7%). A subsequent analysis, approximately 20 minutes later, indicated a concentration of 19.6 ppmv (3.7 ppmv low, or -15.9%). These data indicate that losses to the flux chamber were minimal, although losses to the syringe apparently occurred if significant time elapsed between sample collection and analysis. For the canister sampled, the Varian FID/PID results indicated a concentration of 22.0 ppmv (-1.3 ppmv or -5.6%) based on the mean value for two analyses (20.6 ppmv and 23.4 ppmv). Again, this indicates that the effect of the flux chamber upon sample integrity was minimal.

Physical Parameters

In addition to GC analysis of the soil/waste samples, several physical parameter measurements (e.g., moisture content, porosity, density, etc.) were also made on these samples. Lack of available reference standards appropriate for these measurements precluded conducting performance audits for all parameters except moisture content. The performance audit for this parameter consisted of submitting four audit samples for analysis, along with the field samples. Measurable error was observed for only one of the three samples, and was quite low for that sample (-0.2 wt. % or -1.3%, relative).

REFERENCES

1. Radian Corporation. Evaluation of Air Emissions from Hazardous Waste Treatment, Storage, and Disposal Facilities in Support of the RCRA Air Emission Regulatory Impact Analysis (RIA). Data Volume for Sites 4 and 5, EPA Contract No. 68-02-3171, Work Assignment 63, Austin, Texas, January 1984.

2. Radian Corporation. Evaluation of Air Emissions from Hazardous Waste Treatment, Storage, and Disposal Facilities in Support of the RCRA Air Emission Regulatory Impact Analysis (RIA). Data Volume for Site 6, EPA Contract No. 68-02-3171, Work Assignment 63, Austin, Texas, February 1984.

3. Radian Corporation. Evaluation of Air Emissions from Hazardous Waste Treatment, Storage, and Disposal Facilities in Support of the RCRA Air Emission Regulatory Impact Analysis (RIA). Data Volume for Site 2, EPA Contract No. 68-02-3171, Work Assignment 63, Austin, Texas, March 1984.

4. Wetherold, R.G., and D.A. DuBose. A Review of Selected Theoretical Models for Estimating and Describing Atmospheric Emissions from Waste Disposal Operations. Draft Interim Report, EPA Contract No. 68-02-3171, Work Assignment 63, Austin, Texas, June 1982.

5. Farino, W., et al. Evaluation and Selection of Models for Estimating Air Emissions from Hazardous Waste Treatment, Storage, and Disposal Facilities. Draft Final Report, EPA Contract No. 68-02-3168, Bedford, Massachusettes, October 1982.

6. Radian Corporation. Evaluation and Selection of Models for Estimating Air Emissions from Hazardous Waste Treatment, Storage, and Disposal Facilities. Pretest Site Survey Report, EPA Contract No. 68-02-3171, Work Assignment 63, Austin, Texas, September 1983.

7. Cox, R.D., K.J. Baughman, and R.F. Earp. A Generalized Screening and Analysis Procedure for Organic Emissions from Hazardous Waste Disposal Sites. In: Proceedings of 3rd National Conference and Exhibition on Management of Uncontrolled Waste Sites, Washington, D.C., 1982.

8. Hill, F.B., V.P. Aneja, and R.M. Felder. A Technique for Measurements of Biogenic Sulfur Emission Fluxes. J. Environ. Sci. Health AIB(3), pp. 199-225, 1978.

9. Adams, D.F., M.R. Pack, W.L. Bamesberger, and A.E. Sherrard, "Measurement of Biogenic Sulfur-Containing Gas Emissions from Soils and Vegetation." In Proceedings of 71st Annual APCA Meeting, Houston, TX, 1978, 78-76.

10. Schmidt, C.E., W.D. Balfour, and R.D. Cox. Sampling Techniques for Emissions Measurements at Hazardous Waste Sites. In: Proceedings of 3rd National Conference and Exhibition on Management of Uncontrolled Waste Sites, Washington, D.C., 1982.

11. Code of Federal Regulations, Vol. 45, No. 9, Appendix A, January 1980.

12. Thibodeaux, L.J., D.G. Parker, and H.H. Heck. Measurement of Volatile Chemical Emissions from Wastewater Basins. U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Cincinnati, Ohio, August 1983, EPA 600/2-82-095.

13. Thibodeaux, L.J., D.G. Parker, H.H. Heck, and R. Dickerson. "Quantifying Organic Emission Rates from Surface Impoundments with Micrometeorological and Concentration Profile Measurements." Presented at the Annual Meeting of the American Institute of Chemical Engineers, New Orleans, LA, November 8-12, 1981.

14. Cox, R.D., et al, Evaluation of VOC Emissions from Wastewater Systems (Secondary Emissions), EPA Contract No. 68-03-3038, U.S. EPA, 1983.

15. Perry, R.H., and C.H. Chilton, ed., Chemical Engineers Handbook, Fifth Edition. McGraw-Hill Book Company, New York, New York, 1973.

16. Reid, R.C., J.M. Prausnitz, and T.K. Sherwood, The Properties of Gases and Liquids, Third Edition. McGraw-Hill Book Company, New York, New York, 1977.

17. Cowherd, C., K. Axetell, C.M. Guenther, and G.A. Jutze. Development of Emission Factors for Fugitive Dust Sources. EPA-68-02-0619, June 1974, 197 p.

18. Bohn, R., T. Cuscino, Jr., and C. Cowherd, Jr., Fugitive Emissions from Integrated Iron and Steel Plants. Midwest Research Institute for U.S. EPA, Publication No. EPA-600/2-78-050, March 1978.

19. Thibodeaux, L.J., and S.T. Hwang. Landfarming of Petroleum Wastes--Modeling the Air Emission Problem, Environmental Progress, 1 (1), 42-46 (February 1982).

20. Masser, Charles C. Compilation of Air Pollution Emission Factors, Supplement 12. U. S. Environmental Protection Agency. Research Triangle Park, North Carolina, April 1981.

21. Radian Corporation, Evaluation of Air Emissions from Hazardous Waste Treatment, Storage, and Disposal Facilities in Support of the RCRA Air Emission Regulatory Impact Analysis (RIA). Test Plan/Quality Assurance Project Plan for Sites 4 and 5, EPA Contract No. 68-02-3171, Work Assignment 63, Austin, Texas, September 1983.

22. Radian Corporation, Evaluation of Air Emissions from Hazardous Waste Treatment, Storage, and Disposal Facilities in Support of the RCRA Air Emission Regulatory Impact Analysis (RIA). Test Plan/Quality Assurance Project Plan for Site 6, EPA Contract No. 68-02-3171, Work Assignment 63, Austin, Texas, October 1983.

23. Radian Corporation, Evaluation of Air Emissions from Hazardous Waste Treatment, Storage, and Disposal Facilities in Support of the RCRA Air Emission Regulatory Impact Analysis (RIA). Test Plan/Quality Assurance Project Plan for Site 2, EPA Contract No. 68-02-3171, Work Assignment 63, Austin, Texas, November 1983.